TAMPEREEN TEKNILLINEN YLIOPISTO
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MIKKO RAIKO

REDUCTION OF HEAVY METALS IN WET FLUE GAS SCRUBBERS

Master of Science Thesis

Examiner: D. Sc. Henrik Tolvanen
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ABSTRACT

MIKKO RAIKO: Reduction of Heavy Metals in Wet Flue Gas Scrubbers
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Heavy metal emissions are a significant pollutant in both flue gas and wastewater in power plants. Due to their wide range of health and environmental hazards, research into their behavior in flue gas and reduction in wet scrubbers is of vital importance. In order to understand heavy metal reduction, knowledge has to be supported by speciation and phase behavior in flue gas. In the EU ever increasing emission limits are the driving force behind improvements in heavy metal emission control.

The general aim of this thesis was to investigate heavy metal reduction behavior and efficiencies in wet flue gas scrubbers. This investigation was divided into three different target goals: modeling tool investigation, data survey, and measurement campaign. Modeling tool review was conducted through three approaches: commercial modeling tools, specific and detailed thermodynamic modeling tool, and finally lumped model – tool. The initial idea was to examine heavy metal behavior and sensitivity in flue gas from the furnace outflow to the stack, but due to multiple issues this approach was simplified to only investigate some reduction phenomena. Data survey was performed on existing data, such as publications and previous measurement reports. The idea behind data survey was to find information and measurement data on heavy metal reduction that would support findings from the measurement campaign. Finally, the measurement campaign was conducted in order to examine reduction and heavy metal behavior in a proper, controlled environment and find patterns in behavior and reduction phenomena.

Calculation tools failed to provide a comprehensive modeling tool to investigate heavy metal behavior in flue gas, but some advances were made in reduction prediction. Commercial modeling programs proved to be lacking in heavy metal species and scrubber type data. Thermodynamic and kinetic modeling was incompatible and too complex for the scope of this study, although some useful calculation methods were identified and refined. Lumped model –tool was created to predict heavy metal reduction with data received from data surveys and measurement campaign. Data surveys managed to find some data, which lead to determining average reduction efficiencies for most investigated heavy metals and the data was also used to evaluate heavy metal speciation and phase in flue gas. Data surveys suffered from typical issues, such as measurement inaccuracies, data availability, and comparability. Finally, the measurement campaign was conducted on two combined heat and power plants and five individual cases were measured. Measurement campaign data used failed to provide accurate mass balance evaluations, process parameter sensitivity or cut-off concentrations, but some reduction rates were calculated and heavy metal class behavior identified.

TIIVISTELMÄ

MIKKO RAIKO: Raskasmetallien sitoutuminen märissä savukaasupesureissa
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Avainsanat: märkäpesuri, raskasmetallit, sitoutuminen, savukaasupesuri

Raskasmetallit ovat merkittävä päästö voimalaitosten savukaasu-, ja jätevesivirroissa. Tutkimus niiden käyttäytymisestä savukaasuissa ja sitoutumisesta märkäpesureissa on hyvin tärkeää päästöjen vakavien terveys- ja ympäristöriskien takia. Jotta raskasmetallien sitoutumista pesurissa on mahdollista tutkia, niiden yhdiste- ja faasikäyttäytymistä on ymmärrettävä tarkemmin. Euroopan Unionissa jatkuvasti tiukentuvat raskasmetallien päästörajat ovat päästöjen vähentämisen tärkein ajava voima.

Tämän työn yleinen tavoite on tutkia raskasmetallien sitoutumiskäyttäytymistä ja -tehokkuutta märkäpesureissa. Tutkimus on jaettu kolmeen osaan: laskentatyökalujen tutkimus, mittaustiedonkeruu ja mittauskampanja. Laskentatyökaluja tutkittiin kolmesta näkökulmasta: kaupalliset laskentaohjelmat, termodynaaminen ja kineettinen laskentatyökalu sekä *lumped model* –työkalu. Alkuperäisenä ideana oli tutkia raskasmetallien käyttäytymistä ja herkkyyttä savukaasussa tulipesästä savupiippuun, mutta useiden ongelmien takia tutkimusta yksinkertaistettiin niin, että vain tiettyjä sitoutumisilmiöitä käsiteltiin laskennassa. Mittaustiedonkeruussa käytettiin sekä tieteellisiä julkaisuja, että aikaisemmin tehtyjen mittauskampanjoiden raportteja. Tiedonkeruun tavoitteena oli kerätä tietoa ja mittausdataa raskasmetallien sitoutumisesta sekä tukea tässä työssä tehtyä mittauskampanjaa. Mittauskampanjan tarkoituksena oli tutkia tarkasti raskasmetallien käyttäytymistä savukaasussa ja sitoutumista märkäpesurissa sekä löytää riippuvuuksia näiden välillä.

Laskentatyökalututkimuksen perusteella ei ollut mahdollista löytää tai rakentaa kattavaa työkalua, mutta tiettyjä ilmiöitä raskasmetallien sidonnassa oli mahdollista tutkia. Termodynaaminen ja kineettinen tarkastelu osoittautui yhteen sopimattomaksi ja liian monimutkaiseksi tämän työn puitteissa. Toisaalta, tutkimuksen avulla oli mahdollista määrittää hyödyllisiä laskentatapoja. Kaupallisista laskentaohjelmista tyypillisesti puuttui useita oleellisia raskasmetalliyhdisteitä sekä pesurityyppejä. L*umped model* –laskentatyökalu rakennettiin ennustamaan raskasmetalliyhdisteiden sitoutumista mittaustiedonkeräyksestä ja mittauskampanjoista saadun datan pohjalta. Mittaustiedonkeräyksen avulla saavutettiin kaksi asiaa: lähes kaikkien tutkittujen raskasmetallien keskiarvoisen sitoutumistehokkuuden määritys sekä olomuoto savukaasussa. Mittaustiedon keräämisessä ilmeni tyypillisiä haasteita, kuten mittausepätarkkuudet, tiedon saatavuus ja vertailtavuus. Mittauskampanja toteutettiin kahdella voimalaitoksella, joissa mitattiin yhteensä viisi tasetta. Mittauskampanjasta saadun datan avulla ei onnistuttu laskemaan tarkkoja massataseita, prosessiparametrien herkkyyttä tai raja-arvo konsentraatioita sitoutumistehokkuudelle. Datan avulla oli kuitenkin mahdollista laskea sitoutumistehokkuuksia sekä tutkia tiettyjen raskasmetallien luokituskäyttäytymistä.

PREFACE

This master thesis was written for Power Plant and Combustion Technology research group in Tampere University of Technology. Thesis work was funded by Valmet Technologies, where I have worked as a summer and part-time trainee prior to my thesis work.

Product manager Joonas Arola from the flue gas control business team provided thesis subject and was my thesis coordinator on Valmet side. PhD. Henrik Tolvanen (TUT) was the main coordinator and examiner of my thesis. I would like to thank Henrik, Joonas, and the whole flue gas control team for their help and patience during my thesis work. Their knowledge on the subject and encouraging attitude greatly helped me write this thesis. In addition, the subject of this thesis was challenging and rewarding as it greatly supplemented my studies in TUT.

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" Hundred ideas, ten experiments, one innovation"

Markku Raiko

Tampere, 14.11.2016

Mikko Raiko

CONTENT

TERMS AND ABBREVIATION

BAT	Best available technology
BFB	Bubbling fluidized bed
CFD	Computational fluid dynamics
CHP	Combined heat and power
ESP	Electrostatic precipitator
FF	Fabric filter
HM	Heavy metal
NTP	Normal temperature and pressure
SCR	Selective catalytic reduction
SNCR	Selective non-catalytic reduction
SRF	Solid recovered fuel

A	Frequency of collisions [-]
c_i	Concentration [µg m^{-3}, mg l^{-1}]
D_o	droplet diameter [µm]
D_p	Particle diameter [µm]
E_a	Reaction activation energy [kJ mol^{-1}]
G	Gibbs free energy [J mol^{-1}]
K	Equilibrium constant [-]
k	Kinetic rate constant [cm^3 mol^{-1} s^{-1}]
k_H	Henry's law constant [bar]
K_p	Pressure corrected equilibrium constant [-]
$k_{red\ i}$	Reduction coefficient [-]
L	Ratio of liquid and gas at the inlet [-]
$\dot{m}_i$	Mass flowrate [kg s^{-1}]
$\dot{n}_i$	Mole flowrate [mol s^{-1}]
NTP_{cor}	NTP correction factor [-]
O_{cor}	Oxygen correction factor [-]
P_i	Partial pressure [bar]

P	Pressure [bar]
R	Reynold's molar constant [J mol^{-1} K^{-1}]
T	Temperature [K]
$\dot{V}_i$	Volume flowrate [m^3 s^{-1}]
w_{cor}	Moisture correction factor [-]
x_i	Mole fraction [-]
$x_{solubility}$	Solubility fraction of a substance in water [mol kg^{-1}]
$[X]$	Concentration [mol m^{-3}]
α_i	Activity [-]
η	Reduction efficiency [-]
κ	Venturi constant [-]
λ	Mean free path of gas molecules [nm]
μ_g	Gas viscocity [N s m^{-2}]
μ_i	Chemical potential [J mol^{-1}]
τ	Residence time [-]

1. INTRODUCTION

Pollution control has been a significant part of energy production since the 1970s and is becoming even more important as knowledge in pollution formation and its effects on environmental and human health grows. In addition to scientific advances, legislation also has a significant impact on emission control by introducing emission limits on industrial and power generation plants. In late 20th century, the focus of emission control was on SO_2 and NO_x in order to prevent acidification. More recently, other pollutants, such as greenhouse gases, dioxins, and heavy metals have become more relevant. Although climate change caused by greenhouse gases is the most notable pollution hazard, other types of emissions are sharing its spotlight. Particular focus nowadays is on heavy metal emissions due to their wide range of health risks and transfer pathways.

The control of heavy metal emissions is very important due to their numerous health and environmental effects ranging from neurological and organ damage to cancerous growths in humans and other animals. (Duruibe, et al., 2007; Pandey, 2014) In addition, reduced growth and abnormal growths can be observed in plant life affected by the presence of heavy metals. (Jaishankar, et al., 2014) Such severe environmental effects cannot be ignored and the need to control said emissions has led to EU and national legislature to set limits on allowed heavy metal emissions in gas, liquid, and solid streams exiting industrial or power plants. In this study, the focus is on heavy metal behavior in wet scrubbers, but in order to understand what type of reduction processes need to be examined, heavy metal behavior in flue gas has to be investigated also. This approach includes understanding heavy metal speciation, volatilization, and condensation in flue gas and also their physical and chemical reduction mechanisms in wet scrubbers using sources such as (Abanades, et al., 2002; Meij & te Winkel, 2007; Bao, et al., 2009; Cordoba, 2015)

The goals of this thesis are twofold: to provide data on reduction mechanisms for system development and prevent mistakes in day-today process design of wet scrubbers. By investigating reduction efficiencies, two clear advantages can be achieved. First over or under-designing scrubbers or additional environmental systems can be avoided, thus saving both physical and financial resources. These other systems mainly include additional flue gas cleaning such as active carbon systems or condensate treatment facilities ranging in their purifying intensity. The second advantage is the ability to guarantee a certain level of reduction. In addition to just investigating reduction efficiency, understanding heavy metal reduction mechanisms can lead to both better design solutions and product development. Improving these functions can greatly help wet scrubber effectiveness and competiveness in the face of ever-increasing heavy metal emission limits.

Thesis goals are approached through three different angles: literature review, reduction modeling with calculations tools, and data survey based on existing measurement data and measurement campaigns conducted during thesis work. Literature review will help with a comprehensive overview of heavy metal behavior that can be applied in all the other areas. For example, it can help simplify reduction modeling and calculation tool creation, but also greatly improve analysis of all measurement data. The focus of this thesis will be on selected heavy metals, their behavior in flue gas, and reduction in wet scrubbers. Thesis subject is limited to power plant flue gases, while somewhat focusing on plants using renewable and waste fuels and caustic wet scrubbers. Scrubber type is only narrowed down by data availability in later chapters.

Thesis consists of seven chapters: introduction, four substance chapters, results and discussion, and conclusion. These four chapters discuss the background of heavy metal reduction, reduction modeling and calculation tool creation, data surveys, and finally measurement campaign. Background chapter is divided into three separate portions, where reasons, mechanisms, and devices for heavy metal control are investigated. In comparison to other publications, such as (Cordoba, 2013), a more diverse approach is taken in this thesis. The reasons why heavy metal control is required are separated into three subchapters: EU legislation, health effects on humans, and environmental impact. Subchapter dealing with reduction mechanisms is in four parts: speciation of heavy metals in flue gas, physical reduction phenomena, chemical reduction phenomena, and reduction parameters. The first subchapter is necessary in determining the type and behavior of emissions, i.e. whether it is gaseous or particle-bound. The last subchapter presents parameters affecting reduction mechanisms in order to understand how power plant and wet scrubber operating parameters can influence reduction behavior. Finally, an overview of wet scrubbers, introduction into selected scrubber types, and an overview of balance-of-plant and comparison between wet scrubber designs is presented.

The modeling tool chapter is also divided into three parts: thermodynamic and kinetic modeling, existing modeling tools, and lumped model –tool. Thermodynamic and kinetic modeling chapter presents the attempt to evaluate heavy metal speciation in flue gas, reduction mechanics, and behavior in wastewater This is partly similar to (Aunela-Tapola, et al., 1998; Edwards, et al., 2001). Existing modeling tools chapters investigate the capabilities and potential of commercial calculation software, such as Aspen plus and Chemcad. Finally, lumped model –tool chapter presents a simplified and comprehensive modeling tool to evaluate overall reduction of selected heavy metal. Fourth chapter presents two data surveys: publications, for example (Cordoba, et al., 2012; Ohki, et al., 2011; Tang, et al., 2012) and previous measurement data survey. The fifth chapter is dedicated to the measurement campaigns performed during this thesis. Data from chapters four and five is analyzed separately, but comparisons are drawn where deemed useful. Both of these chapters also contain reduction efficiency evaluation, which produces general heavy metal reduction values based on the data used.

2. BACKGROUND

In this chapter the theoretical background on heavy metal reduction is discussed from three different points of view: why reduction is needed, how it is conducted, and what type of equipment can be used to achieve it. In the first subchapter European Union legislation and directives on heavy metal pollution and the health effects of heavy metals on human physiology and the environment, i.e. plants and other animals are examined. The following subchapter investigates different phenomena involved in heavy metal reduction and also studies the fate of heavy metals in combustion processes. Last subchapter deals with the scrubbing system and its variations.

2.1 Legislation and physiological impact of heavy metals

2.1.1 European Union legislation on heavy metals

This subchapter deals with the legislative side of heavy metal emission control by investigating the role of EU legislation in creating responsibilities for industrial and energy production plants. This legislation is presented in the form of directives set by the EU parliament. More precisely the directives on industrial emissions and pollution emissions from large combustion plants are the guiding pieces of legislation. These directives set up limits on emissions, define BAT-systems (best available technology), and monitors to determine whether plants are following their legal requirements. (Eurlex, 2010; Eurlex, 2015)

As an example, Table 1 contains current limits on heavy metal emissions for waste incineration plants received from the current directive. Values in brackets are lower emission limits presented the latest BAT reference document. These documents influence the direction and future of emission legislation and are indicators of future emission limits. BAT-documents present emission limit windows for local authorities, who can decide a national limit. These ranges can be large, for example 0.001 – 0.015 [mg l^{-1}] in wastewater for mercury, and 0.01 – 1 [mg l^{-1}] for most heavy metals. Ranges in flue gas are 0.2 – 10 [µg nm^{-3}] for mercury and for most heavy metals it is 0.075 – 0.3 [µg nm^{-3}]. Figure 1 presents the reduction in emissions of certain heavy metals. (CENTRE, 2013)

Table 1: *Current emission limits for heavy metal substances in waste incineration plants* (Eurlex, 2015; CENTRE, 2013)

Heavy metal and its compounds	Emission limit in wastewater [mg l^{-1}]	Emission limit in flue gas [mg nm^{-3}]
Mercury (Hg)	0.03 (0.001)	0.05 (0.0002)
Cadmium (Cd)	0.05 (0.01[(1)])	0.05 (0.0008) [(1)]
Thallium (Tl)	0.05 (0.01[(1)])	0.05 (0.0008) [(1)]
Arsenic (As)	0.15 (0.01[(2)])	0.5 (0.075) [(2)]
Lead (Pb)	0.2 (0.01[(2)])	0.5 (0.075) [(2)]
Chromium (Cr)	0.5 (0.01[(2)])	0.5 (0.075) [(2)]
Copper (Cu)	0.5 (0.01[(2)])	0.5 (0.075) [(2)]
Nickel (Ni)	0.5 (0.01[(2)])	0.5 (0.075) [(2)]
Zinc (Zn)	1.5 (0.01)	-
[(1)] Limits describe the sum of all group concentrations (Cd + Tl) [(2)] Limits describe the sum of all group concentrations (As + Pb + Cr + Cu + Ni)		

The impact of heavy metal emission legislation can be observed in Figure 1. In this graph, the emission rates of cadmium, lead, and mercury are presented.

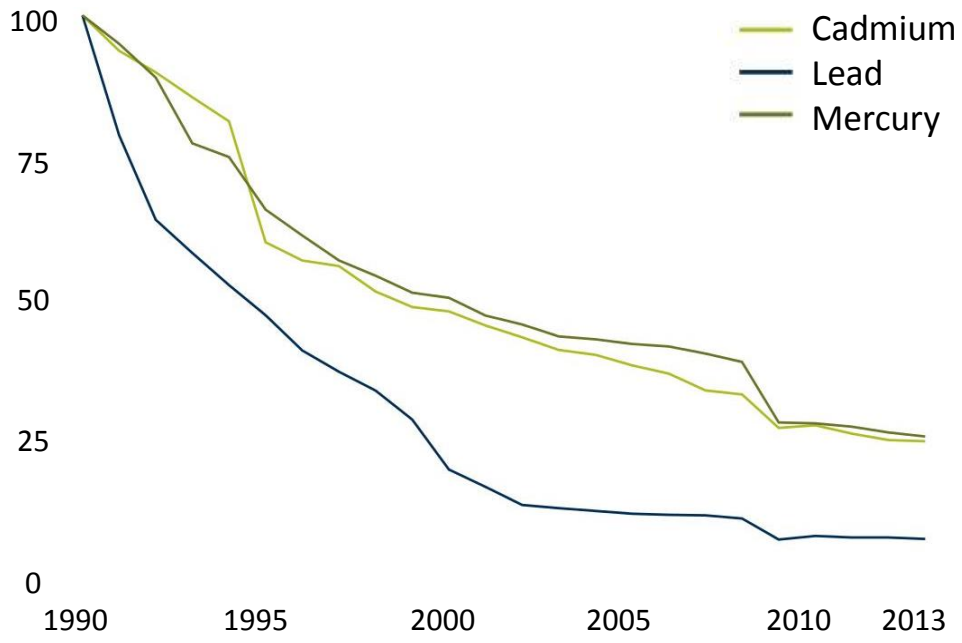

Figure 1: *Development of certain heavy metal emissions (Cd, Pb, Hg) in the EU (y-axis presents reduced emission values)* (EEA, 2015)

These examples provide a way to understand how legislation influences heavy metal emissions and how effective it has been. Ever tightening limits on emissions and the requirement to use best available technology (BAT) in controlling emissions is the driving force in reducing heavy metal emissions.

2.1.2 Health effects of heavy metals on human physiology

Heavy metals have a wide range of different adverse effects on human well-being depending on the type of heavy metal. Typical routes of exposure include air, food, and water pollution, although in the scope of this study air pollution from combustion sources is more important. Heavy metal air pollution is also a significant threat to human health due to its ability to disperse quickly on a wide area and having a simple method of contact. (Kampa & Castanas, 2008; Järup, 2003) Although heavy metals are dangerous to humans even in low concentrations, some of them are necessary for day-to-day functions in human body. For example, zinc is important for male reproductive health, calcium in metabolism, also magnesium and arsenic have a dietary importance in trace quantities. Many heavy metals only have adverse health effects, for example: cadmium, mercury, and lead. (Duruibe, et al., 2007)

Heavy metals can cause a wide range of varying illnesses and damage to different organs. They typically affect the nervous system and muscles in humans in a way similar to Alzheimer's or Parkinson's disease. Heavy metals damage organs such as liver, kidneys, brain, and lungs. Different heavy metals have their own characteristic effect on human health. Arsenic, e.g., is a dangerous substance in its inorganic form, since it is very carcinogenic, forming cancerous growths in lungs, kidneys, and can cause skin cancer. Other chronic symptoms of arsenic intake are changes in skin pigmentation and lesions. More acute effects in low quantities include nausea, blood vessel damage and a change in heart rhythm. In larger quantities, arsenic is very deadly due to changes it causes in vital organs. (Jaishankar, et al., 2014)

Cadmium affects primarily the kidneys and lungs, but also affects bone structure by reducing bone density. It is unclear whether kidney damage caused by cadmium is reversible, but in chronic cases cadmium can cause end stage renal disease. Carcinogenic effects of cadmium are still unclear due to studies showing both positive and negative correlation between cadmium and cancer. (Järup, 2003)

Chromium is highly toxic and carcinogenic in some of its oxidized forms (VI) but also necessary trace element in others (III). Chromium (VI) forms very toxic compounds with other metals such as lead, calcium and strontium. Chromium (VI) compounds can cause serious internal and external damage to tissue and leave behind a very slowly healing wound or ulcer. It is shown that chromium can affect the replication and transcription of DNA. This can lead to cancerous growths. (Jaishankar, et al., 2014)

Mercury can form both inorganic and organic compounds that are both dangerous to humans. Inorganic mercury has a litany of both acute and chronic effects. Acute effects cause lung damage and chronic effects can cause neural damage and symptoms, such as tremor, restlessness, and change in personality. Other chronic effects include kidney damage, carcinogenic impact, and allergic reactions. Organic mercury compounds also

damage the nervous system, and it can also lead to heart disease. (Jaishankar, et al., 2014; Järup, 2003)

Lead has a wide array of neurological effects on humans. In acute cases, they range from headache and restlessness to psychosis and hindered mental capacity. Chronic exposure can cause memory and mental issues, lesions in neural pathways, and kidney damage. Lead can have great adverse effects in cognitive development of children. It can cause unwanted behavior and significant learning difficulties. (Järup, 2003) Table 2 contains a summary on the effects of heavy metals on human physiology.

Table 2: *Adverse effects of heavy metals on human physiology* (Kampa & Castanas, 2008; Duruibe, et al., 2007; Jaishankar, et al., 2014; Järup, 2003)

Heavy metal	Carcinogenic	Organ damage	Chronic effects	Acute effects (low quantity)	Acute effects (high quantity)
Arsenic (As)	highly	lungs, kidneys, skin	skin pigmentation and lesions	nausea, heart rhythm change, blood vessel damage	Severe organ failure
Cadmium (Cd)	probably	lungs, kidneys, bone structure	end-stage renal disease		Pulmonary effects
Chromium (Cr)	highly	pulmonary tract, skin	slowly healing ulcers	deep wounds	deep wounds
Mercury (Hg)	highly	kidneys, lungs, heart	tremor, anxiety, depression		neural and lung damage, vomiting, nausea
Lead (Pb)	possibly	nervous system, kidneys	memory loss, reduced mental capacity, lesions, kidney damage		headache, stomach pain, neural damage, psychosis

2.1.3 Environmental impact of heavy metals

This subchapter deals with the impact of heavy metals on the environment. In this study the effect of heavy metals on fish, animal, and plant populations are investigated. Heavy metals are toxic and carcinogenic substances as was demonstrated in the previous subchapter. They have similar effects on other animals as well and they can damage plant structure and inhibit nutrient in-take. Typical types of heavy metal pollution consist of aerosols, gaseous heavy metals, and dissociated heavy metals in sewage. (Nagajyoti, et al., 2010; Pandey, 2014)

In addition to the effects of heavy metals on human physiology described in the previous chapter, they also have properties affecting other organisms in general. Heavy metal toxicity and carcinogenic properties are significantly enhanced by the effect of bioaccumulation. Bioaccumulation occurs when an organism takes in substances that are not removed through usual metabolic processes and instead build up inside the organism or have to be neutralized through distinct mechanisms some organisms have evolved. Heavy metals have another mechanism to affect organisms, nutrient displacement. This mechanism primarily affects the metabolism of plants. Heavy metals have a great impact on plant well-being, because not only are heavy metals toxic and bio-accumulative, they also displace vital nutrients from the soil. This leads to a multi-layered crisis for the plant, since it is taking in toxic substances, not removing them through normal metabolic functions, and is also deprived of nutrients. (Singh, et al., 2011)

The effects of heavy metal toxicity have similarities between human and other animal physiologies, but health effects of other animals have to be considered in a broader way. Typical signs of heavy metal toxicity in animals are abnormal growths, poor overall condition, and reduced immunity. Mercury and lead can be found to cause severe neurological symptoms in animals, such as wandering in a circle, light sensitivity and other issues such as a lack of important trace elements. (Pandey, 2014)

Fish are very susceptible to the adverse effects of heavy metals. These effects are similar when compared with humans and other animals. For example, arsenic and cadmium compounds cause very aggressive and often deadly cancerous growths. Mercury also has devastating effects on the physiology of fishes. Effects include reduction in glucose transfer, deformities, neurological symptoms (convulsions), and change in behavior. Chromium also affects metabolic functions (protein and cholesterol levels) in fishes. (Pandey, 2014)

Plants are also greatly affected by a presence of heavy metals in the soil and air. Typical symptoms include growth reduction, deficiency in nutrient in-take, and disturbances in the development of the plant. Cadmium causes several visible changes in plants physical appearance, for example leaves and roots turning brown and reduction in growth. It also reduces chlorophyll production and affects the in-take of essential nutrients such as iron and nitrates. Some plants on the other hand can handle arsenic quite easily. This can be achieved by effectively changing the composition of arsenic to a less toxic form. However, it can still be dangerous, if the plant matter is used for food. (Nagajyoti, et al., 2010)

The presence of chromium affects the seed production of plants greatly. This poses a significant threat to the well-being of a plant population. As do all heavy metals, so does Chromium affect root growth but it distinctly reduces the length of roots and also disrupts plants photosynthesis, electron transport and enzyme activities. These metabolic

changes create a need for additional detoxification processes within the plant to reduce heavy metal concentrations. (Nagajyoti, et al., 2010)

Mercury is extremely toxic to plant life in all of its forms, but its ionic form has to greatest impact due to its biological and physical effects. Physical effects include blocking the flow of water inside the plant by binding proteins. Biological effects include disruption on a cellular level and causing the plant's detoxification processes to begin, thus creating an unnecessary load on the plant. (Nagajyoti, et al., 2010)

Lead is a readily available toxin and it has a wide array of harmful effects on plant life. These effects range from inhibition of seed production, enzymes and photosynthesis. It also reduces root and leaf growth and can create abnormal growths in cell walls and roots. (Nagajyoti, et al., 2010) The combination of these disruptions with availability in soil and air, heavy metal compounds are a significant threat to the well-being of the environment. Table 3 contains a summary on the effects of heavy metals on the environment.

Table 3: *Adverse effects of specific heavy metals on the environment (In case of an empty cell, see human physiology)* (Nagajyoti, et al., 2010; Pandey, 2014)

Heavy metal	Effects on animal physiology	Effects on fish physiology	Effects of plant physiology
Arsenic (As)		highly aggressive cancer	Easily detoxified by some plants
Cadmium (Cd)		highly aggressive cancer	reduced growth, reduces nutrient in-take
Chromium (Cr)		anemia, changes in protein levels	reduced growth and development
Mercury (Hg)	changes in behavior, nutrient deficiency	illness, deformities, death, tremor, anorexia	disrupting water flow, oxidative stress
Lead (Pb)	changes in behavior, nutrient deficiency		reduced growth, abnormal growths

2.2 Phenomena in heavy metal reduction

2.2.1 Fate of heavy metals in flue gas

In order to understand the reduction of heavy metals, the physical and chemical phenomena regarding the generation, speciation, and reactions of heavy metal compounds in the combustion process. This subchapter is dedicated to studying the fate of heavy metals in flue gas before they arrive at the scrubber system. This information defines the situation for actual reduction mechanisms, which are discussed in the following subchapters.

There are many mechanisms for transfer of heavy metals from the fuel source. The main mechanism affecting heavy metal distribution is volatilization. Volatilized substances have significantly better mobility and therefore have a greater impact on emissions. Heavy metals and their compounds volatility is influenced by temperature, ash generation, and reactions with other compounds. If substances are not volatilized they can still cause emissions through ash particles. Non-volatile heavy metal compounds can be found in ash and other particle matter. They tend to distribute between bottom and fly ash. Heavy metals enriching in bottom ash are typically non-volatile and form easily removed compounds, such as sulfates and oxides. Bottom ash only contains heavy metal compounds that are not volatilized, but fly ash contains both non-volatilized and volatilized compounds in most cases. Fly ash and other particles are transferred to flue gas by entrainment. In this process, heavy metals can also be transferred to flue gas without volatilization. Although non-volatilized heavy metals can be found in fly ash, more characteristic method for heavy metal enrichment in fly ash exists. This method involves the condensation of volatilized heavy metal compounds on the surface of particle matter, when flue gas is cooled by post-combustion heat transfer. Typically, heavy metals that form aluminosilicates, sulfates, or have interactions with organic compounds can be found in fly ash. (Querol, et al., 1995; Zhang, et al., 2008)

Because there are many different pathways, process parameters, and compounds affecting heavy metal emission formation and distribution, classifications have been made to simplify the process of emission evaluation. Heavy metals and their compounds can be classified in three different classes based on their behavior during combustion: non-volatile compounds, volatile compounds that condense after flue gas has cooled, and finally volatile compounds that are not condensed in the plant. They are grouped up in classes 1, 2, and 3, respectively. Since heavy metal behavior depends significantly on the compound and other process parameters, it is difficult to create absolute distinctions for heavy metal species. A general classification of certain heavy metals has been made for this thesis and it is presented in Figure 2. (Cotton, et al., 2014; Fernandez, et al., 1992; Meij & te Winkel, 2007)

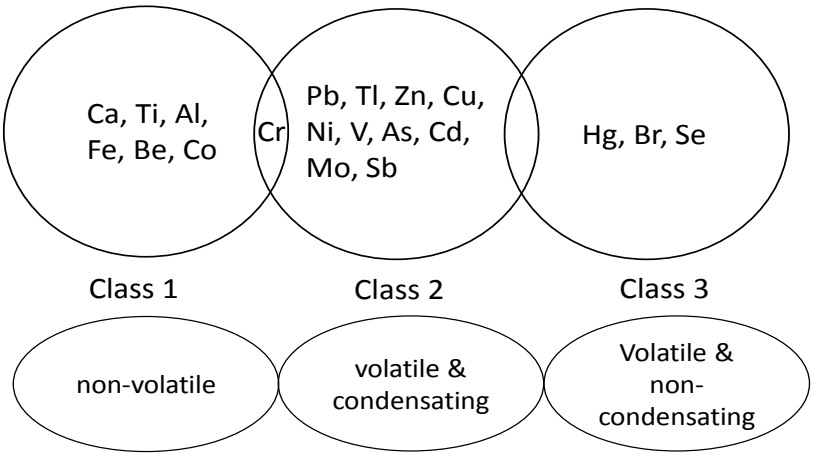

Figure 2: *Heavy metal behavior classification in combustion* (Cotton, et al., 2014; Fernandez, et al., 1992; Meij & te Winkel, 2007)

As described previously, the compound form of heavy metals has a great impact on their behavior in flue gas. Vaporization of heavy metals is directly affected by their chemical composition, especially the condensation temperature. Changes in this composition can drastically alter the volatilization and condensation behavior of certain metals. A case in point is the significant increase in volatility for most metal compounds if there is chloride present in flue gas. Chloride replaces the oxygen in metal oxides and metal chlorides are formed. These metal chlorides have a significantly higher condensation temperature, i.e. they stay longer in vapor form. In low quantities of chloride, it affects lead first before oxidizing other heavy metals. There is also a possibility for the formation of heavy metal compounds that contain class 2 heavy metals in solid form at very high temperatures. An example of this type of substance is $NiCr_2O_4$, which is solid even in 1900 K temperature. The determination of heavy metal behavior in flue gas can be complex due to the large number of interactions between different substances in flue gas. (Linak & Wendt, 1993)

In addition to metal compound composition and temperature, particle matter has a noteworthy effect on the condensation process. Characteristic mechanisms for class 2 heavy metal behavior in flue gas include: condensing on particle matter, adsorption to particle matter, and homogenous nucleation. First mechanism happens when heavy metal substances vapor pressure is reduced under its partial pressure. This happens when flue gas is cooled enough. The second mechanism can occur in higher temperatures because it is not controlled by vapor pressure. Adsorption can lead to further chemical reactions on the surface of the particle. The third mechanism is influenced by vapor pressure. This mechanism occurs primarily when there is not enough surface area (particle matter) to condensate on. Now heavy metals form nuclei homogenously and these tiny nuclei coagulate into submicron particles. (Cotton, et al., 2014; Linak & Wendt, 1993)

The behavior of mercury has to be examined separately due to its classification (class 3) and importance in emission control. Mercury is considered to exist in three different phases: Hg^P in particles, Hg^0 as elemental gaseous mercury and finally Hg^{2+} as oxidized mercury substances, for example $HgCl_2$ and HgO. Hg^P is behavior similar to class 1 and condensed class 2 heavy metals and will not be discussed in this paragraph. Mercury that is not contained in particles typically vaporizes as Hg^0 and as temperature drops a portion oxidizes to mercury oxide or chloride. There is no condensation mechanism involved in the fate of class 3 heavy metals, but they can be adsorbed by particle matter such as active carbon. Since adsorption is possible for elemental mercury, its oxidation can happen heterogeneously as well as homogeneously. Elemental gaseous mercury can also be oxidized by SCR-catalysts used in NO_x reduction. (Sun, et al., 2015)

Figure 3 shows an overview of the fate of heavy metals in flue gas. In addition, it describes the different phenomena involving reduction in wet scrubbers as an introduction to following subchapters.

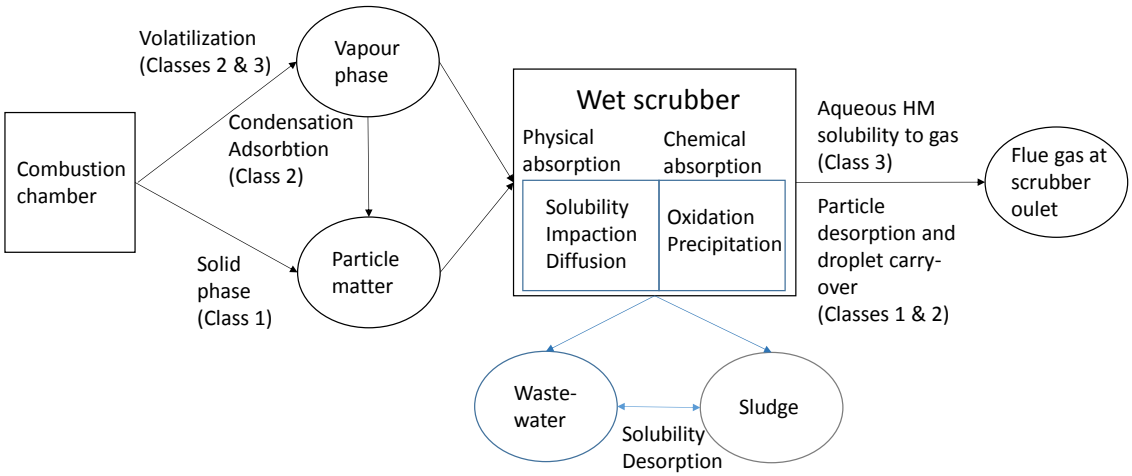

Figure 3: *General overview of the transfer and reduction mechanisms of heavy metals* (Abanades, et al., 2002; Linak & Wendt, 1993; Cotton, et al., 2014; Fernandez, et al., 1992; Bao, et al., 2009; Mohan, et al., 2008; Cordoba, 2015; Fang, et al., 2012)

2.2.2 Physical reduction mechanisms

The key aspect of discussing the reduction of heavy metals is to understand the mechanisms that govern the process. This subchapter deals with physical phenomena involved. These mechanisms consist of solubility, inertial impaction, interception, and diffusion. First mechanism affects the reduction of gases and the other three are phenomena dealing with the reduction of particle matter. Gaseous emissions are collected when they are absorbed in to the scrubbing liquid and dissolve. In order to be dissolved gas molecules have to travel through film layers to reach the surface of the liquid. There

are film layers in both the gaseous and liquid phase. (Howard E. Hesketh, 1995) Gas solubility is controlled by natural laws such as Henry's and Raoult's law. Henry's law states that

$$P_i = k_H * x_i \quad (1)$$

in which P_i [bar] is partial pressure of the solute, k_H [bar] is a characteristic constant and x_i [mol l^{-1}] is the mole fraction of the solute. This law correlates the effect of pressure on solubility. Raoult's law investigates the effect of the solvent on the vapor pressure of the solution. Gaseous emissions are primarily reduced through this method but it can also affect heavy metals in absorbed particles. In addition to pressure, solubility is influenced by parameters such as temperature, molecular structure, and pH. (Zumdahl & DeCoste, 2013; Li, et al., 2013) Gaseous heavy metals (class 3), such as elemental and oxidized mercury, are typically reduced through solubility. Although elementary mercury is insoluble to water, oxidized mercury is easily captured. Through experimental data it has been determined that gaseous mercury reduction is also influenced by pH but temperature does not have a large impact. (Bao, et al., 2009; Diaz-Somoano, et al., 2007)

Particle reduction in wet scrubbers is primarily controlled by inertial impaction. In this method particles are captured in the scrubbing liquid droplets in a fairly simple way. When a flue gas stream faces a droplet, the gaseous phase goes around it, but inertial forces are slowing the particle matter enough to force it to impact on the surface of the droplet. This impact causes the particle to be absorbed into the droplet. Interception also acts as a reduction mechanism for larger particles. This method describes the opposite situation to impaction. Interception occurs when a droplet impacts a particle instead of a particle impacting a droplet. These reduction methods are greatly affected by particle size, because larger particles are less likely to move with the flue gas fluently and are larger targets for droplets. Other parameters influencing reduction include droplet size and velocity difference between the particle and the droplet. Diffusion collection is based on the Brownian movement of small particles and motion of fluids. Random movement of molecules due to internal energy causes these movements. This added movement is not the most significant reduction pathway, but it needs to be accounted for because diffusion has a more significant impact on smaller particles such as submicron and condensed particles. (EC/R-Incorporated, 1998; Howard E. Hesketh, 1995)

There are also other methods targeted at the reduction of smaller particles. These smaller particles have a tendency to be more toxic and dangerous to human health in general due to heavy metal condensate on their surface and the somewhat unhindered transfer of said particles in flue gas. Condensation reduction is based on the idea of having water vapor condensing on small particles and increasing their size. Even a growth of some microns in the particle diameter can increase the reduction process significantly by allowing traditional particle reduction, i.e. inertial impaction take place. (Fan, et al., 2009;

Mohan, et al., 2008) Figure 4 describes the different particle reduction mechanisms in wet scrubbers.

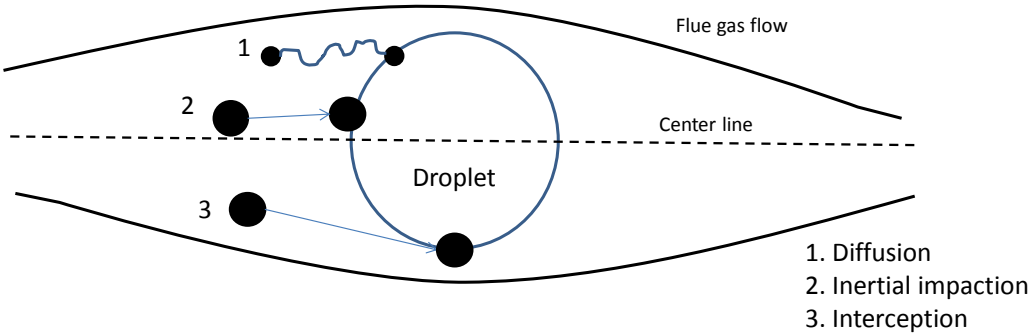

Figure 4: *Particle reduction mechanisms in wet scrubbers* (Howard E. Hesketh, 1995)

2.2.3 Chemical reduction mechanisms

In order to fully understand the reduction processes, the chemical aspect has to be investigated as well. It is very significant because reactions change the composition and parameters of both the flue gas and the scrubbing liquid. Even the primary function of wet scrubbing is based on chemical reactions. The typical purpose for wet scrubbers is to remove sulfur dioxide and acidic gases from flue gas. This reduction is achieved by using sorbent chemicals to bind sulfur and other substances to form solid sludge and/or wastewater that contains unwanted elements. There are many types of scrubbing techniques, for example wet and dry scrubbing, and possible regeneration of scrubbing liquid by another chemical cycle. In this thesis, the focus will remain on wet scrubbing. Before any chemical reactions can take place, physical absorption of particle matter and dissolution of gases needs to happen. Now both the sorbent and the emission compound are in the same liquid phase. Typical sorbents used include limestone ($CaCO_3$, CaO) in limestone scrubbers and different sodium compounds (NaOH, Na_2CO_3, Na_2SO_3) in alkaline (caustic) scrubbers. Overall chemical reactions for these reduction processes are

$$CaCO_3(s) + SO_2(g) + 2\ H_2O(aq) \rightarrow CaSO_3{\bullet}2H_2O(aq) + CO_2(g) \quad (2)$$

$$CaSO_3{\bullet}2H_2O(aq) + \frac{1}{2}\ O_2(g) \rightarrow CaSO_4{\bullet}2H_2O(s) \quad (3)$$

for the limestone desulfurization process and

$$2\ NaOH(aq) + SO_2(g) \rightarrow Na_2SO_3{\bullet}2H_2O(aq) + H_2O(l) \quad (4)$$

$$Na_2CO_3(s) + SO_2(g) + 2\ H_2O(aq) \rightarrow Na_2SO3{\bullet}2H_2O(aq) + CO_2(g) \quad (5)$$

for alkaline (caustic) scrubbing. Alkaline scrubbing process can be modified into a regenerative process by regenerating sodium sulfite with CaO or $CaCO_3$. (Cordoba, 2015)

Sodium hydroxide can also be used to neutralize acidic components in gases such as hydrochloric acid. Reduction mechanism

$$NaOH(aq) + HCl(g) \rightarrow NaCl(aq) + H_2O(aq) \quad (6)$$

involves the chemical reaction between an acid and sodium hydroxide and it produces sodium chloride and water. (Carlsson, 2008)

Although most heavy metal emissions are contained through physical particle absorption, some chemical reactions between class 1 & 2 heavy metals, sorbent, and desulfurization products may occur. This type of reduction is called precipitation and it is similar to limestone desulfurization process: reaction 3. The goal in precipitation is to form solid emission particles in scrubber wastewater and remove them with filtration systems. Two typical pathways have been identified: hydroxide and sulfide precipitation. In hydroxide precipitation heavy metals react with calcium or sodium hydroxide and form solid particles in high base conditions (pH 9.5 – 12). Sulfide method can precipitate heavy metals on a wider pH scale but in acidic conditions heavy metal sulfides can cause H_2S emissions. (Fu & Wang, 2011; Kilpinen & Zevenhoven, 2004)

Mercury control chemistry has to be discussed separately due to its unique principles. As previously discussed mercury emissions can be categorized into three different groups. However, in this paragraph only the chemical reactions of Hg^0 and Hg^{2+} in wet scrubbers are investigated. First of all, elemental mercury cannot be captured in its pure form due to its insolubility to water. Thus catalytic reactions are needed in order to oxidize mercury. Characteristic catalytic substances, for example compounds V_2O_5 and WO_3 with TiO_2 structure catalyze the oxidization of Hg^0 into Hg^{2+} which then can dissolve into the scrubbing liquid and undergo various chemical reactions. It is shown previously in this subchapter that sulfur dioxide is bound as sulfite–ions (SO_3^{2-}) in the scrubbing liquid. These ions can react with oxidized mercury and water to reduce Hg^{2+} back into elemental mercury. Reactions reducing Hg^{2+} into Hg^0 are particularly troublesome since the emission happens after going through the capture process and cannot be handled afterwards. (Sun, et al., 2015)

Improved oxidation and re-emission prevention are key aspects in improving mercury capture. Elemental mercury can also be oxidized by the scrubbing liquid itself, if the correct sorbent is added and process parameters are met. For example, using $KMnO_4$ as an oxidizer in acidic conditions can lead almost up to 70% removal of Hg^0. Also the formation of $Hg(SO_3)_2^{2-}$ and $HgSO_4$ leads to more stable substances that prevent re-emission of oxidized mercury in its elemental form. This can be achieved by having more sulfur-ions that are available and excess oxygen in the scrubber. (Fang, et al., 2013; Fang, et al., 2012) Different approaches to elemental mercury reduction have been made by using $NaClO_2$ as an oxidizer in the sorbent. After oxidization, mercury can further react with nitric acid or chloride-ions to form mercury nitrate or mercury

chloride, respectively. Although these compounds do not precipitate and bind mercury into a solid form, they also do not lead to reactions that might release Hg^{2+} back to gaseous elemental mercury. (Krzyzynska & Hutson, 2012)

2.2.4 Reduction parameters

This subchapter contains an overview of different aspects of the overall phenomena involved that influence the reduction of heavy metals. Table 4 contains a list of previously discussed mechanisms and the parameters impacting their performance.

Table 4: *Reduction mechanisms and sensitivity parameters of different reduction mechanisms in wet scrubbers* (Howard E. Hesketh, 1995; Zumdahl & DeCoste, 2013; Cordoba, 2015; Fu & Wang, 2011; Kilpinen & Zevenhoven, 2004; Krzyzynska & Hutson, 2012; Fang, et al., 2012; Charlatchka & Cambier, 2000)

Reduction mechanism	Sensitivity parameters
Particle reduction	particle and droplet size and their difference in velocity, temperature affecting diffusion movement, pressure drop, inflow velocity (condensation steam flowrate, if available)
Gas solubility	pressure, temperature, pH(acidic),
Chemical reactions (excluding heavy metal reduction)	sorbent reactivity, temperature, pH
Chemical reactions of heavy metal reduction (excluding mercury)	temperature, pH(base)
Chemical reactions of mercury reduction	temperature, pH(acidic), sorbent type, SO_2 concentration

In all cases expect particle reduction the composition of flue gas and scrubbing liquid influences the different reactions taking place in the system. Cross-referencing all the interactions between different species present in such a complex system dilutes the overall understanding and creates a large number of special situations best suited to be examined in a case-by-case basis.

2.3 Wet scrubbers

2.3.1 Technical overview

A significant part in understanding heavy metal emission control is to understand the available devices and systems. This subchapter describes the basic functionality and general design of wet scrubbers. Wet scrubbers remove and contain emissions by forc-

ing flue gas in contact with liquid droplets or surfaces. The physical and chemical reduction mechanisms have been described in previous chapters. Wet scrubbers are used to remove both soluble gases and particle matter, although the optimal conditions are very different for these emission reduction methods. When compared to other devices, wet scrubbers have both positive and negative aspects. The positive side includes:

- Smaller size leads to convenient placement and capital cost reduction
- Dust re-emissions are very unlikely
- Ability to handle hot and wet gas
- Multipollutant control

The negative side has the following:

- Corrosion by acid solutions
- Significant power consumption leads to higher operating costs
- Wastewater and sludge disposal and recovery issues

Scrubbers have in addition to emission control the ability to recover heat by cooling and also condensing flue gases as they come in contact with water droplets in the scrubber. Water condensed from the flue gas is now added to the liquid circulation, but some water vapor escapes and causes a plume when exiting the stack. The scrubbing process also produces a waste stream in the form of used scrubbing liquid that contains particle matter, precipitated, and soluble substances. Heavy metals are a significant component in this hazardous liquid and create a requirement to also control both aqueous emissions and solid sludge from wet scrubbers. (Pence, 2012)

2.3.2 Different wet scrubber types

The typical and most basic scrubber type is the spray tower or chamber, where nozzle on the top of the chamber sprays droplets on the flue gas flowing through the chamber. In this method the spray nozzles handle the atomization of droplets. Now the water droplets present absorb pollutants from the flue gas through mechanisms described in the previous subchapter and pools on the floor of the chamber. A spray scrubber can operate in a vertical or horizontal position and it can also handle any flue gas feed-in configuration. These configurations consist of cocurrent, countercurrent and cross-current flows. In a cocurrent flow flue gas and droplets travel in the same direction, in countercurrent model they travel in opposite directions, and finally in cross-current model flue gas moves tangentially in regard to the droplets. Spray scrubbers can reach a cut diameter of 2 μm by using nozzles that form droplets in the 100 – 500 μm range. (Flagan, 1988) Typical set-up for gas and droplet flow is countercurrent configuration. Upsides of spray chambers are small capital cost and pressure drop and downsides include low efficiency and high carry-over. (Kumar, et al., 2011) In Figure 5 can be found the overall design of a spray tower scrubber.

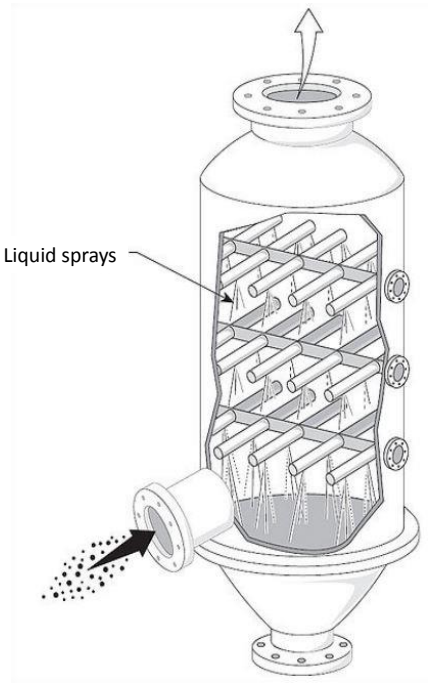

Figure 5: *Countercurrent spray tower* (Cooper & Alley, 2011)

Venturi scrubbers are a more special case in scrubber design and they are used in removing very small particles (under 2 μm in diameter). These scrubbers are effective enough that they can be considered reasonable alternatives to bag house filters and electrostatic precipitators in certain cases, such as inflammable, acidic or sticky gas handling.

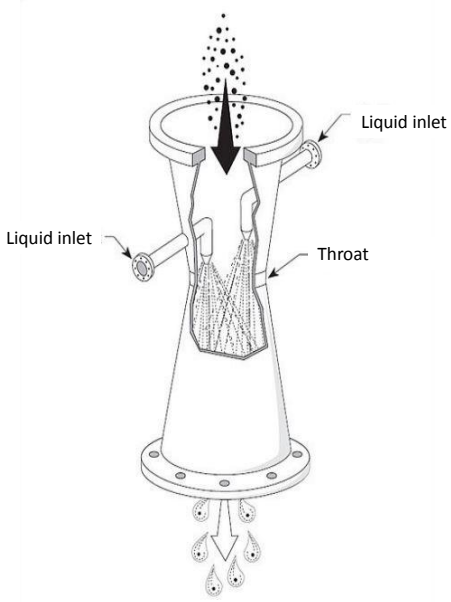

Figure 6: *Venturi scrubber* (Cooper & Alley, 2011)

As can be seen in Figure 6, venturi scrubber has three different parts: inlet, throat and the expander. (Cheremisinoff, 1993) The inlet is shaped like a diffusor to accelerate inflowing flue gas. The flue gas flows in through the inlet and reaches the throat where most of the absorption mechanisms take place. Accelerated flue gas flow is very turbulent in the throat area of the scrubber thus increasing mixing between flue gas and droplets. (EC/R-Incorporated, 1998) There are two types of throat design: wetted and non-wetted. In the wetted design scrubbing liquid is not sprayed in to the gas but instead it's injected to the walls around the inlet and flows down to the throat as a film. The flue gas flowing by at a great velocity then atomizes this film. Through atomization venturi scrubber forms small droplets that can absorb pollutants from the flue gas. Non-wetted method uses nozzle spraying or injecting to bring to liquid straight to the throat. The scrubber in Figure 6 is a non-wetted nozzle spray venture scrubber.

After the venturi throat flue gas reaches the expander where it's slowed down by the expanding shape of the scrubber and slowed down. The point of this design feature is to reduce frictional losses from turbulence and also recover kinetic energy from the flue gas movement. If flue gas velocity is low enough expander may not be necessary to reduce turbulent friction. One drawback present in venturi scrubbers in the risk of clogging. This may occur when flue gas flowrate is too high, contains a great deal of particle matter, or precipitated substances. Advantages of venture scrubbers include simple design and maintenance; they are also superb at removing small particles. Disadvantages consist of clogging and a large pressure drop that leads to higher energy requirement. (Cheremisinoff, 1993)

Packed-bed scrubbers are similar to spray tower in some ways, but packed-bed scrubbers have fewer liquid feed-in points and have packing material inside the chamber. The purpose of this packing material is to increase the surface area of gas-particle interaction with liquid. Scrubbing liquid is fed in the chamber from above the packed-bed and it coats the material in a liquid film. Packed-bed scrubbers can be used in vertical countercurrent configuration or in horizontal cross-flow configuration. (EC/R-Incorporated, 1998) Figure 7 describes packed-bed scrubber design and the mist eliminator in the upper part of the chamber will be discussed in the next subchapter.

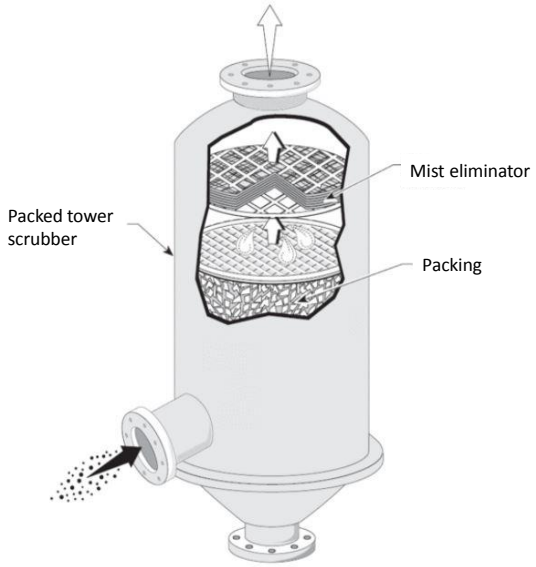

Figure 7: *Packed-bed scrubber* (Cooper & Alley, 2011)

Countercurrent configuration has a great advantage in pollution capture, because in it more used scrubbing liquid is exposed to dirty flue gas and unused liquid with cleaner flue gas. This means that physical and chemical phenomena are more balanced throughout the chamber, in other words concentration gradients are formed favorably within both the flue gas and the scrubbing liquid. This is a significant boost in emission collection, particularly when capturing low-solubility gases. Comparing countercurrent and cross-current scrubbers, certain general rules about cost can be determined. Countercurrent packed-bed scrubbers have lower capital cost, but higher operation cost in comparison to cross-current counterpart. Operating costs are increased by a higher scrubbing liquid flowrate and greater pressure drop.

The type of pollution reduction required influences packing material design. For example, dissolution and chemical absorption is enhanced by greater reaction area, but particle collection is increased by having packing material that forces the flue gas stream to go around it, thus creating a chance for particle impaction between packing material and particle matter. Packing material can vary from plastic and glass to ceramics and metal. Packed-bed can also be mobile or stationary, i.e. packing components can move in the bed or be completely stationary. Packing shapes include berl and intalox saddles, pall rings, and tellerette packing. Packed-bed scrubbers excel at reducing emissions through physical (dissolution) and chemical reactions, for example hydrogen chloride and ammonia. Particles over 5 µm are reduced, but smaller particles require condensation reducing in order to be captured. This requires an additional cycle discussed in the following paragraph. (Cheremisinoff, 1993)

Condensation scrubbers are used to collect submicron particles. As stated in the previous paragraph this method can be integrated to other scrubbers, for example packed-bed scrubbers. Condensation scrubbing consists of three phases. Scrubbing begins with

cooling flue gas to saturation point with water. Next steam is injected into the chamber and it becomes supersaturated, then it begins to condense on submicron particles. Last phase is the collection of these small particles that have been grown by condensation of steam. Particles can now be captured by traditional reduction methods. (EC/R-Incorporated, 1998)

2.3.3 Balance of plant and functionality of different wet scrubbers

In this subchapter, the different support systems and devices that are used to support wet scrubbers are investigated. The most significant component supporting wet scrubbers is mist eliminator that is used to prevent carry-over of liquid droplets. These can be cyclonic or centrifugal devices, but the most common method is to use inertial impaction. Impaction collection is conducted by using a mesh or a pad that droplets impact onto. These mesh eliminators can reach a reduction of 99% if flue gas velocity is within the operating limits. (Howard E. Hesketh, 1995) Other components required include pumps and fans. Pumps are used to move fresh scrubbing liquid to the chamber and wastewater away from the bottom of the chamber. Fans are used to maintain the velocity of the flue gas in order to have the optimal reduction environment. Another important support system is wastewater treatment. This system purifies the scrubber wastewater by precipitating aqueous substances and filtering solid components out of the stream. After used scrubbing liquid has been treated it can be recirculated back into the scrubber or released to the environment. Depending on the composition of the sludge, it can be used as a reagent in some industrial processes or disposed in a waste handling center, depending on its toxicity. (EC/R-Incorporated, 1998) As an overview of this subchapter, table 5 contains the reduction capabilities of different scrubber types. It contains information already presented in previous paragraphs but has some new details as well.

Table 5: Overview of pollutant control by scrubber type (EC/R-Incorporated, 1998; Howard E. Hesketh, 1995; Cheremisinoff, 1993; Linak & Wendt, 1993; Pence, 2012)

Scrubber type	Particle reduction size	Advantages	Disadvantages
Spray scrubber	2-10	low capital cost and pressure drop	low efficiency, carry-over
Venturi scrubber	0.5-2	reduction of small particles, handling of problematic substances in gases	clogging, high energy demand
Packed-bed scrubber	5-10	excellent reduction through chemical reactions and dissolution	packed-bed plugging by particle matter
Condensation scrubber	submicron	capture of heavy metal condensation particles	requires steam as an additional inflow

3. MODELING TOOLS

This chapter is dedicated to presenting the different modeling approaches, tools, and results acquired in this research. The goal was to find or create a modeling tool that can handle heavy metal emissions in all their forms and also model reduction interactions in order to determine overall reduction of heavy metal components in a certain type of wet scrubber and varying process parameters. In addition, a sensitivity analysis was to be conducted using said modeling tool. Due to the complex behavior of heavy metal in flue gas this proved very challenging. Findings will be presented next by beginning with a thermodynamic and reaction kinetic observation for select phenomena in the reduction process. Discussion can be found in chapter 6.1. Next existing modeling tools (Aspen plus and Chemcad) were examined and tested. In the final subchapter, a lumped model – tool is created based on data collected in the Data survey chapter.

3.1 Thermodynamic equilibrium and kinetic modeling

3.1.1 Theoretical overview

The idea of the speciation and chemical reduction modeling tool was based around investigating thermodynamic equilibrium of certain chosen reaction paths and thus determining the composition of heavy metal compounds in flue gas, different chemical reduction processes, and in wastewater. Right from the start a great problem arose; there were simply too many heavy metal substances to model, therefore thermodynamic and kinetic modeling was only tested on mercury and its compounds as a proof of concept and to test the usefulness of the method. Another goal of this tool was to investigate the sensitivity of mercury reduction and speciation in different temperatures and pressure.

Thermodynamic equilibrium can be an effective tool to determine stable components in different chemical processes. In order to determine heterogeneous and homogenous equilibriums an equation linking reaction parameters and component composition is required. Equation 8 represents the equilibrium equation for the reaction described in equation 7.

$$Hg(g) + \frac{1}{2} O_2(g) \leftrightarrow HgO(g) \tag{7}$$

$$K = \frac{[HgO]}{[Hg][O_2]^{0.5}} \tag{8}$$

Where K [-] is the equilibrium constant in the temperature the reaction occurs. The term [X] [mol l^{-1}]is the concentration of a certain substance. By assuming the gas investigated has ideal behavior pressure can also be added as a process parameter by using activity as instead of concentration. These equations are presented in equations 9 and 10.

$$\alpha_i = \frac{P_i}{P_{tot}} \tag{9}$$

$$K_p = \frac{P_{HgO}}{P_{Hg}{P_{O2}}^{0.5}} {P_{tot}}^{-0.5} \tag{10}$$

Equation 9 is used instead of concentrations in equation 8 and the difference stoichiometric constants are used as the exponent for P_{tot} [bar]. P_i [bar] stands for components partial pressure and P_{tot} for total pressure and K_p [-] is the equilibrium constant where also pressure is considered. (Zumdahl & DeCoste, 2013)

Now that the equilibrium equation has been defined, a way to determine a temperature dependency for equilibrium constant needs to be determined. The calculation is based around the idea of using Gibbs free energy. The calculation of equilibrium constant was based around equation 11 and 12. Again by using the reaction in equation 7 as an example the Gibbs free energy of a reaction can be defined by using chemical potential and stoichiometric constants. The equation

$$\Delta G_{reaction} = \mu_{HgO} - \mu_{HgO} - 0.5\mu_{O2} \tag{11}$$

where μ_i [J mol^{-1}] is the chemical potential of a substance and they are multiplied by the stoichiometric constants of the reaction in question. (Mulder, 2004)

In order to tie in $\Delta G_{reaction}$ [J mol^{-1}] with K and to reach a temperature dependent constant equation 12 is required. Equation

$$lnK_p(T) = -\frac{\Delta G(T)_{reaction}}{RT} \tag{12}$$

where R [J mol^{-1} K^{-1}] is molar gas constant and T [K] is the temperature of the system. It has to be noted that K_p and $\Delta G_{reaction}$ are temperature dependent themselves in addition to the parameter T. (Ronis, 2015)

Another approach can also be used in determining K_p. Instead of using Gibbs energy of the reaction, the Gibbs energy of formation for substances in the reaction can be used and equilibrium constant can be defined for every components question. With these equilibrium constants the determination of the equilibrium constant for the reaction can be achieved with equation 13.

$$logK(T) = logK(T)_{HgO} - logK(T)_{Hg} - 0.5logK(T)_{O_2} \tag{13}$$

In this equation K_i is the equilibrium constant for a certain substance calculated using the formation Gibbs energy. (Barin, 1989)

In addition to thermodynamic modeling a brief kinetic approach was also taken to determine the speciation of mercury in flue gas. Kinetic modeling takes into account the time, which is something that cannot be investigated with thermodynamics alone. By determining whether reactions occur fast enough compared to the residence time of the flue gas the relevance of said reactions can be estimated. Again by using equation 7 as an example reaction rate can be defined as

$$\frac{d[HgO]}{dt} = k[Hg]^m[O_2]^n \quad (14)$$

where k [$cm^3\ mol^{-1}\ s^{-1}$] is the kinetic rate constant and m and n are experimental exponents. In order to determine k(T) Arrhenius equation is needed. This equation determines how many reagent collisions lead into the reaction taking place. Equation

$$k = Ae^{-\frac{E_a}{RT}} \quad (15)$$

where A [$cm^3\ mol^{-1}\ s^{-1}$] is the number of collisions of reactive molecules and E_a [$J\ mol^{-1}$] is activation energy. Variable A represents the number of reactions taking place without considering reaction temperature dependency. Activation energy is used to calculate a fraction of collisions that can lead to a reaction in said temperature. By using these to equations the significance of the reaction in terms of reaction time can be established. (Zumdahl & DeCoste, 2013)

3.1.2 Overview of the modeling tool

As described earlier the main purpose of the modeling tool was to predict speciation of mercury compounds in flue gas, estimate reduction for different mercury compounds in the scrubber, and finally to determine the composition and complexation of dissociated mercury. First part used both thermodynamic and kinetic data but the two following parts only used thermodynamic data.

Creation of the tool began by defining correlation functions for equilibrium constants. Data used in these functions typically correlated log K values with temperature. In some cases log K values were unavailable and thus $\Delta G_{formation}$ or $(\Delta G_{formation}\ (RT)^{-1})$ values were correlated with temperature. Log K values were used to keep the actual values in a manageable range. In table 6 the type and source of data has been listed.

***Table 6**: Species used in thermodynamic modeling and their data sources*

Compound	Correlated value	Source	Compound	Correlated value	Source
Hg(g)	log K	(Barin, 1989)	O_2 (g)	log K	(Barin, 1989)
$HgCl_2$ (g)	log K	(Barin, 1989)	SO_2 (g)	log K	(Barin, 1989)
HgO (g)	log K	(Barin, 1989)	H_2O(g)	log K	(Barin, 1989)
$HgSO_4$ (s)	log K	(Barin, 1989)	NaCl(aq)	$\Delta G_{formation}$ $(RT)^{-1}$	(Spitzer K. S., 1984)
HCl (g)	log K	(Barin, 1989)	NaOH(aq)	$\Delta G_{formation}$ (Constant value)	(Kotz & Treichel, 2005)
H_2SO_4 (l)	log K	(Barin, 1989)	H_2O(l)	$\Delta G_{formation}$ (Constant value)	(Kotz & Treichel, 2005)

Next the log K and temperature data was correlated and equations were created by using temperature as a variable. There are a couple of examples of these correlations in Figure 8.

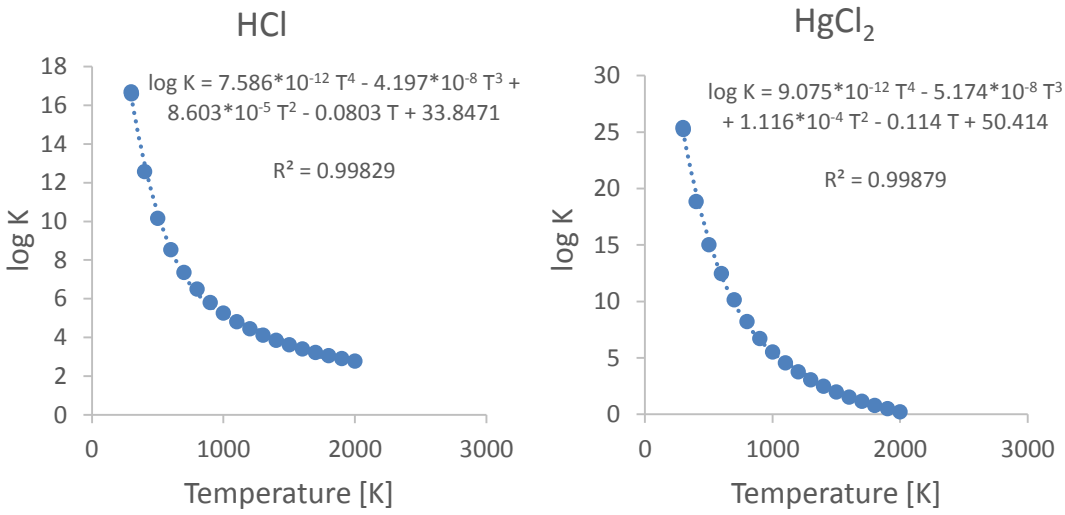

***Figure 8:** Examples of correlations created between log K and temperature values*

In these graphs there are also correlation functions and their accuracy (R^2). Also the solubility of Hg and $HgCl_2$ was investigated by plotting Henry's constant and solubility, respectively with temperature. Similar correlation functions to previously described log K were created. Data for these correlations was acquired from (Clever, et al., 1985). In addition, a similar investigation was made into the behavior of aqueous mercury compounds and their complexation. Equilibrium data used was received from (Feng, 2003).

After gathering the data and creating the correlations, the actual calculation begins. Initially a more overall chemical reaction pathway was examined to try and validate the concept and also find out preliminary sensitivity data in terms of concentration of species, temperature, and pressure. Mercury speciation in flue gas and chemical absorption was investigated by using equation 7 and the following 4 equations.

$$HgO(g) + 2\,HCl(g) \leftrightarrow HgCl_2(g) + H_2O(g) \tag{16}$$

$$HgCl_2\,(g) + SO_2(g) + 2\,NaOH(aq) + \tfrac{1}{2}\,O_2(g) \leftrightarrow HgSO_4(s) + 2\,NaCl\,(aq) + H_2O(l) \tag{17}$$

$$HgO(g) + SO_2(g) + \tfrac{1}{2}\,O_2(g) \leftrightarrow HgSO_4(s) \tag{18}$$

$$HgSO_4(s) + H_2O(l) \leftrightarrow Hg(g) + H_2SO_4(l) + \tfrac{1}{2}\,O_2(g) \tag{19}$$

Equations 10 and 13 are used to calculate equilibrium constant and the concentrations for each species involved in these reactions. After this the remaining Hg and $HgCl_2$ are investigated using the solubility of $HgCl_2$ and Hg by using equation 20 and 1, respectively. Equation

$$\dot{n}_{solute} = x_{solubility}\dot{m}_{solvent} \tag{20}$$

where $\dot{n}_{solute}$ [mol s^{-1}] is the molar flowrate of mercury chloride dissociated in water, $\dot{m}_{solvent}$[kg s^{-1}] is the mass flowrate of water in scrubbing liquid, and $x_{solubility}$ [mol kg^{-1}] is the fraction of mercury chloride that can dissociate in water at a certain temperature.

Finally the behavior of aqueous oxidized mercury and its complexation was briefly examined by using the same principle as was used for equations 7, 16-19. Equations 21 – 24 are some examples of complexation phenomena that were investigated. Data used in these calculations was acquired from (Feng, 2003) and it correlates reaction equilibrium constant log K with temperature.

$$Hg^{2+} + 4\,Cl^- \leftrightarrow HgCl_4^{2-} \tag{21}$$

$$Hg^{2+} + H_2O \leftrightarrow Hg(OH)^+ + H^+ \tag{22}$$

$$Hg^{2+} + OH^- \leftrightarrow Hg(OH)_2 \tag{23}$$

$$Hg^{2+} + 2\,H_2O \leftrightarrow Hg(OH)_2 + 2\,H^+ \tag{24}$$

A wider range of reaction pathways is available but, was not used in this study due to preliminary issues in modeling.

Also a brief investigation into the kinetic modeling of the gas phase was performed by investigating Arrhenius equation data from (Edwards, et al., 2001). An attempt was made to simplify the modeling with the help of chemical reactions and some Arrhenius equation data from (Sliger, et al., 2000). Kinetic modeling was designed using the following reactions:

$$Hg + Cl_2 \rightarrow HgCl_2 \quad (25)$$

$$Hg + Cl \rightarrow HgCl \quad (26)$$

$$HgCl + HCl \rightarrow HgCl_2 + H \quad (27)$$

$$HgCl + Cl_2 \rightarrow HgCl_2 + Cl \quad (28)$$

$$H + Cl_2 \rightarrow HCl + Cl \quad (29)$$

$$HgCl + Cl \rightarrow HgCl_2 \quad (30)$$

In (Edwards, et al., 2001) data collision frequency A was corrected by multiplying it with T^a term in some cases. In most cases the calculation was performed with equations 14 and 15.

3.2 Existing modeling tools

3.2.1 Brief overview of software

Existing commercial modeling tools such as Aspen Plus v8.6 and Chemcad v6.5.7 were investigated in this study. The investigation of these tools was based around the idea of using them to create a detailed modeling tool that can handle a large number of heavy metal species and is able to predict reduction in different scrubber types. Also these tools can be used to investigate some of the interactions between other gas components and heavy metal compounds and also heavy metal behavior in wastewater. Both of these programs are based around traditional chemical engineering, such as reactor calculations, distillation, heat transfer, and also separation techniques, where Aspen Plus has more petrochemical calculation blocks and Chemcad is more focused on heat transfer. Functional basis in both of these programs is the same: there are streams and calculation blocks. Streams contain information regarding the inflow and outflow of material. Typical information includes a set of selected components, flowrates, temperature, and pressure. Both of these programs have a wide range of flue gas components to be added to the inflow stream and they can also predict ionic behavior in liquid streams. Each calculation block has inflow and outflow streams, and their parameters are changed by the calculations in the block. For example, there are reactors, distillation columns, heat exchangers, and of course separation devices. In the following subchapters different mod-

eling cases regarding the scope of this study are presented. All calculations conducted in the following two subchapters were not included in the results and discussion chapter, since these calculations are only examples pointing out different deficiencies and issues in the functionality of existing modeling tools.

3.2.2 Modeled cases in Chemcad

There are two cases modeled in Chemcad: solubility of elemental mercury in scrubbing liquid and particle reduction calculation using a venturi scrubber block. These simulations do not represent the overall heavy metal reduction, but instead some interesting parts due to challenges faced during modeling. In subchapter 2.2.1 the speciation of heavy metals was discussed and it was found that class I & II heavy metals tend to be mostly found in particle matter. Also class III heavy metals mainly stay volatilized and are reduced through solubility. A more detailed modeling was not achieved and reasons for this will be explained later.

Solubility case of mercury was investigated by using a flash reactor, two inflow and outflow streams. Flash reactor calculation is based on thermodynamic equilibrium and it calculates the equilibrium conditions in preset temperature and pressure. The inflow stream compositions can be found in table 7.

Table 7: *Solubility case: inflow streams*

Process value	Gas stream	Liquid stream
T [˚C]	150	15
p [bar]	1.00	1.00
$\dot{n}_{N2}$ [mol h^{-1}]	100.00	
$\dot{n}_{CO2}$ [mol h^{-1}]	100.00	
$\dot{n}_{H2O}$ [mol h^{-1}]	20.00	800.00
$\dot{n}_{SiO2}$ [mol h^{-1}]	20.00	
$\dot{n}_{SO2}$ [mol h^{-1}]	50.00	
$\dot{n}_{HCl}$ [mol h^{-1}]	5.00	
$\dot{n}_{Hg}$ [mol h^{-1}]	50.00	
$\dot{n}_{O2}$ [mol h^{-1}]	20.00	
$\dot{n}_{NaOH}$ [mol h^{-1}]		1 - 10

This gas and scrubbing liquid composition is arbitrary but a key detail is the presence of hydrochloric acid (HCl) in gas stream. It will dissociate into the scrubbing liquid lowering its pH significantly when sodium hydroxide (NaOH) stream is small. These two components and other ionic compounds in wastewater cause buffering phenomena that can be observed in the results. Figure 9 contains the Chemcad flowsheet used in this simulation.

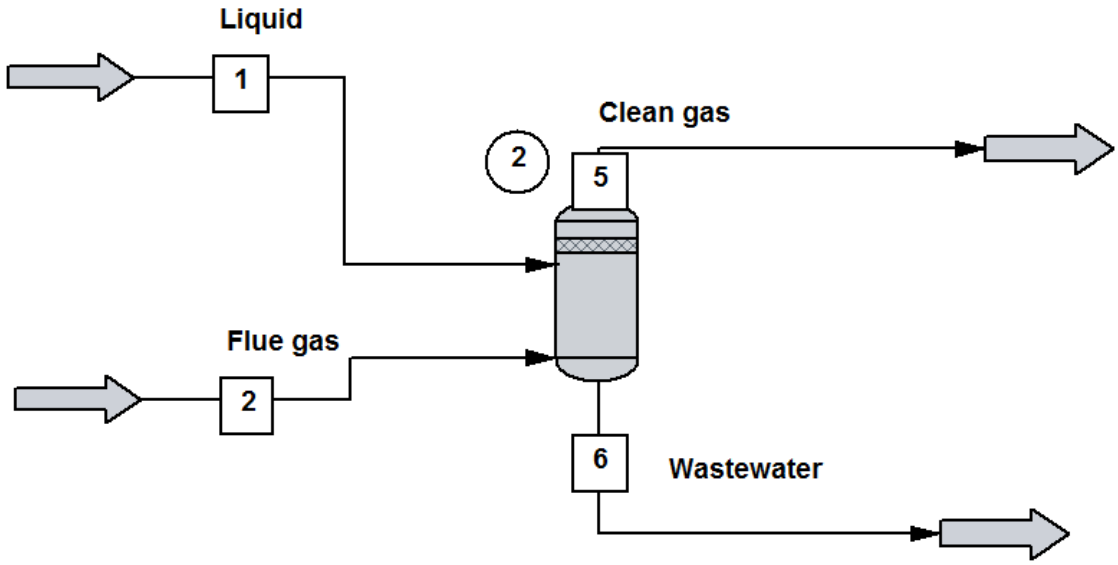

Figure 9: *Elemental mercury solubility calculation flowsheet using a flash reactor*

In flash calculation block equilibrium parameters pressure and temperature were also changed, so that pressure remained at 1 bar and temperature changed from 50˚C to 90˚C. The resulting data was plotted in figure 10.

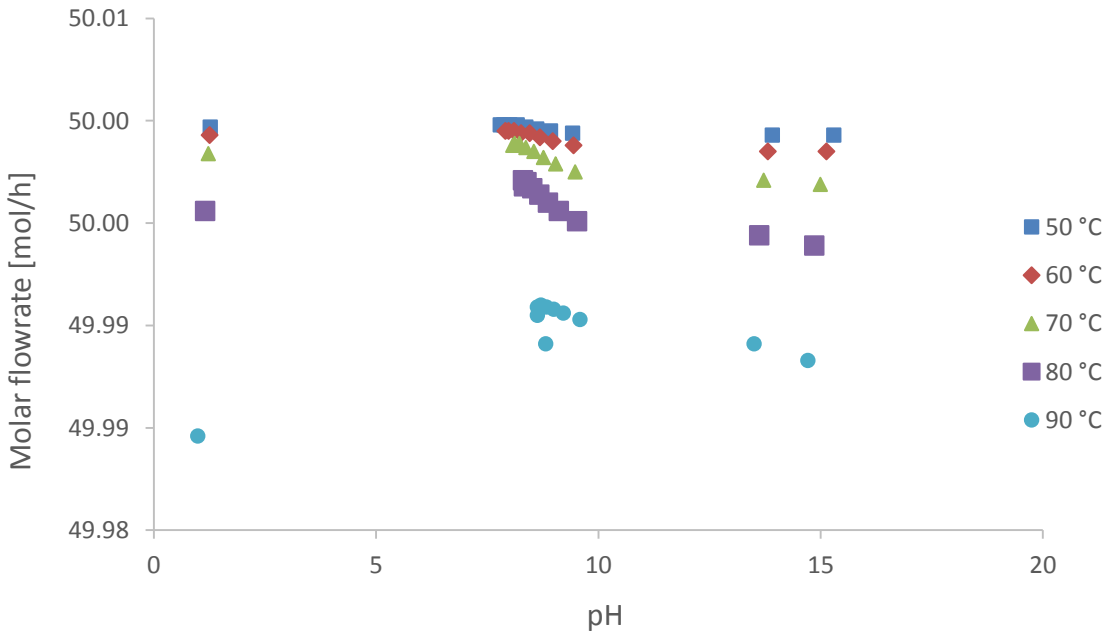

Figure 10: *Sensitivity analysis of elemental mercury solubility*

The legend in Figure 10 refers to the temperature stages set in the flash block and x-axis represents pH, and y-axis the mole flowrate of elemental mercury in wastewater. Data points are calculated by evenly changing the sodium hydroxide mole flow from 1 to 10. From Figure 10 three points of interest are found: influence of pH and temperature on

solubility and also the very large portion of mercury in wastewater even though it should be insoluble. Elemental mercury solubility is inversely affected by temperature which was also confirmed by calculations in 4.1.2. The effect of pH is not as clear due to the large leap in acidic range and the buffering effect observed. At higher levels, the effect of pH seems more significant, but any clear correlations cannot be formed based on this data. Solubility seems to be higher at base and even higher near neutral conditions, but when temperature is lower, acidic conditions seem more favorable and neutral conditions remain the most optimal. Main issue in this calculation has to do with the mole flowrate of mercury in wastewater. Elemental mercury should be very insoluble in water, but almost all of it (99.96% at lowest) is dissolved in to the aqueous stream.

The other case involved modeling venturi scrubber's particle reduction. This modeling predicts the reduction of class I and II heavy metals. It is assumed that their compounds have condensed on particle matter, thus their reduction should depend very heavily on particle reduction. In this case a large number of different substances are not used to model the solid phase stream, but instead a single component is chosen to represent them. This component is silicon oxide (SiO_2). The reduction efficiency is calculated by using the following 4 equations. The main equation is

$$\eta = 1 - e^{(-\kappa L \psi^{0.5})} \tag{31}$$

where η is the reduction efficiency, κ [-] is venturi constant, L [-] is the ratio of liquid and gas at the inlet, and ψ [-] is calculated with equation 32

$$\psi = \frac{C \rho_p V_g D_p^{0.5}}{18 D_0 \mu_g} \tag{32}$$

where C [-] is a correction factor, ρ_p is particle density, V_g [m s^{-1}] is gas velocity, D_p [µm] is particle diameter, D_o [µm] is droplet diameter, and μ_g [N s m^{-2}] is gas viscosity. The correction factor C is calculated with equation 33

$$C = 1 + \frac{2A\lambda}{D_p} \tag{33}$$

where λ [nm] is the mean free path of gas molecules and A [-] is

$$A = 1.257 + 0.4e^{\frac{-1.1 D_p}{2\lambda}} \tag{34}$$

The calculation block uses these equations and input values to evaluate the reduction efficiency for solid particles. (Chemstatios, 2012)

Just as in the previous case, there is a calculation block (venturi) and two inflow and outflow streams. The venturi scrubber block has two input values: throat diameter and venturi constant. Values used are 0.1 m and 1000, respectively. Venturi constant can range from 750 to 1500. Values used for inflow streams and results of this calculation

can be found in Table 8. The total inflow of flue gas was 1000 [kmol h^{-1}] and for liquid 3630 [kmol h^{-1}]. Total outflow was 883 [kmol h^{-1}] for clean gas and 3921 [kmol h^{-1}] for wastewater. It has to be noted that all the ionic compounds have been cut out from this list due to the large number of components.

Table 8: *Stream values of Chemcad modeling case for venturi scrubber*

Process value	Flue gas	liquid	Clean gas	Wastewater
T (˚C)	150	15	77.627	77.627
p (bar)	1	1	1	1
X_{H2O}	0.05	0.9	0.349058	0.811664
X_{N2}	0.47		0.532469	2.55E-06
X_{CO2}	0.2		0.046298	4.41E-05
X_{O2}	0.05		0.056645	4.85E-07
X_{SiO2}	0.17		0.01553	0.039855
X_{HCl}	0.03			2.55E-08
X_{SO2}	0.03			
X_{NaOH}		0.1		

Particle distribution in this simulation had 21 groups of fixed particle diameters ranging from 1 to 200 μm i.e. (1, 10, 20…190, 200). Each of these groups had an equal mass fraction of 0.0476. The flowsheet used in calculations can be found in Figure 11.

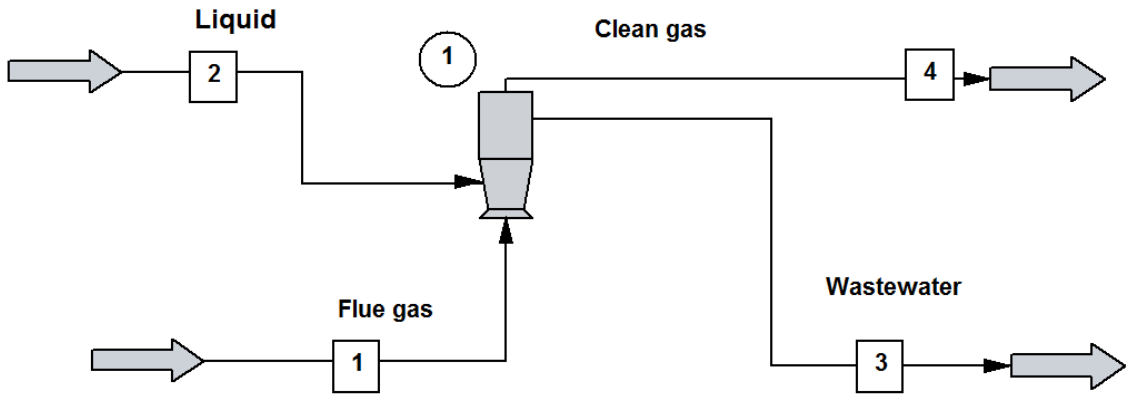

Figure 11: *Venturi scrubber modeling flowsheet in Chemcad*

It can be seen that reduction efficiency is only dependent on physical parameters such as particle diameter and gas velocity. These parameters are not directly affected by the composition of incoming gas or liquid flow. Parameters affecting reduction in this case include calculation block input values, total flue gas and liquid stream flowrate, particle distribution function, and finally temperature and pressure can have a minor effect on gas viscosity. Reduction efficiency of 92% was achieved in this study. It should also be noted that this calculation block takes into account gas absorption, which can be seen by observing oxygen and nitrogen in wastewater.

3.2.3 Modeled cases in Aspen Plus

Aspen Plus was used for two simulation cases: venture scrubber and spray tower particle reduction. This program was also only used to simulate certain aspects of heavy metal reduction due to the deficiencies in program databases and availability of calculation blocks. Both of the calculation cases examined here deal with the reduction of solid components i.e. class I & II heavy metals. A more detailed modeling might be achieved by small changes in calculation blocks, a more comprehensive component list, and the addition of a wastewater speciation calculation in a new block.

Venturi scrubber calculations were made similarly to the calculations conducted in the previous subchapter using Chemcad. Expect that in this case solid components were actual heavy metal compounds instead of silicon oxide. Flowsheet consists of two inflow streams, two outflow streams, and one calculation block. This same flowsheet is used in the next case but the block is changed from venturi to spray tower. Figure 12 shows the flowsheet used in every Aspen plus modeling case.

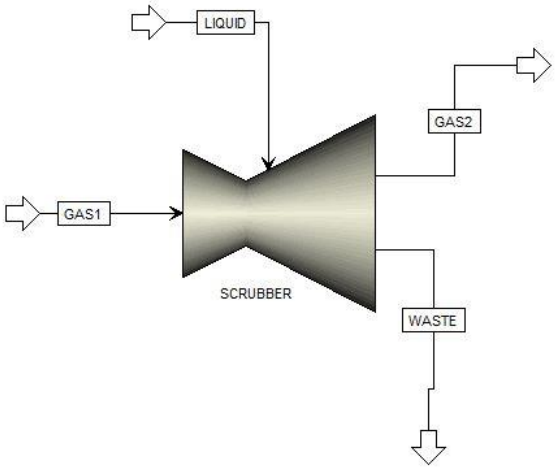

Figure 12: *Flowsheet used in Aspen plus modeling*

In the venturi scrubber case, block input values included throat design, diameter, and length. These values are round, 0.1 m, and 1 m, respectively. Throat diameter can also be replaced by using gas velocity at venturi inlet. Since Chemcad and Aspen plus have different input values for venturi calculations, a comparison on species level is not assumed accurate or useful. Due to this fact, only the particle density function is kept similar to estimate the reduction efficiency. Because Aspen plus handles solid components as their own substream, stream data compiled here is merged from these two substreams. Gas 1 stream a total flowrate of 780 [kmol h^{-1}], Gas 2 had 743 [kmol h^{-1}], liquid stream had 593 [kmol h^{-1}], and finally waste stream 630 [kmol h^{-1}]. Table 9 contains data for input streams and also result streams. NaOH dissociates in water, but ionic components were neglected in this table due to the very large number of components. Particle density function was created by having 10 particle diameter windows that all

contain equal mass fraction. Windows are 20 μm large and start from 0 μm (0-20, 20-40…180-200) and every window has the mass fraction of 0.1.

Table 9: *Input values and results of input and output streams for venturi case*

Process value	Gas 1	Gas 2	Liquid	Waste
T [˚C]	150	57.54231	15	57.54231
p [bar]	1	0.9569357	1	0.9569357
X_{H2O}	0.184527	0.170607	0.909015	0.883687
X_{CO2}	0.125893	0.132025		1.81E-05
X_{NaOH}			54.0039	54.0039
X_{N2}	0.59334	0.622312		2.22E-06
X_{O2}	0.069259	0.072641		4.69E-07
X_{Pb}	0.001114	9.97E-05		0.001262
X_{PbO}	0.000965	8.64E-05		0.001093
X_{Zn}	0.00353	0.000316		0.003997
X_{Cu}	0.003633	0.000325		0.004113
X_{Cd}	0.002054	0.000184		0.002325
X_{CdO}	0.001798	0.000161		0.002036
X_{Cr}	0.00444	0.000397		0.005027
X_{Zn}	0.00353	0.000316		0.003997
X_{ZnO}	0.002836	0.000254		0.003212
X_{As}	0.003081	0.000276		0.003489

From this data it can be determined that calculation does not differentiate between solid components and every solid component is being reduced from the gas 1 stream with the same efficiency. Reduction efficiency calculated for this case is 91.5%. The heavy metal components seen in this table is the full extent of heavy metals and their species found from Aspen plus databases. Particle reduction is not solely based on calculation block input values, but also affected by the temperature and pressure of inflow streams. Calculations also take into account gas solubility in water as can be seen from the very small mole fractions present in waste stream.

The spray tower case uses the same inflow stream values and only one solid component, because solid particle reduction is not effected by the component. Spray tower block also has different input parameters. These parameters consist of relative gas velocity or the diameter of droplets, nozzle orifice diameter, spray angle, and finally the number of nozzles. In these case the values selected were: 5 [m s^{-1}] relative gas velocity, 0.1 m for nozzle orifice diameter, spray angle was 180˚, and there were 10 nozzles. Also particle density function remains the same as in previous case but the total flowrates have been altered: Gas 1 stream a total flowrate of 759 [kmol h^{-1}], Gas 2 had 687 [kmol h^{-1}], liquid stream had 2374 [kmol h^{-1}], and finally waste stream 2446 [kmol h^{-1}]. Table 10 contains the stream input and result values for spray tower calculation case.

Table 10: *Input values and results of input and output streams for spray tower case*

Process value	Gas 1	Gas 2	Liquid	Waste
T (˚C)	150	48	15	48
p (bar)	1	1	2	1
X_{H2O}	0.187497	0.10448	0.909015	0.909052
X_{CO2}	0.127919	0.14254		2.07E-05
X_{NaOH}			0.090985	0.088053
X_{N2}	0.60289	0.672137		2.66E-06
X_{O2}	0.070374	0.078456		5.75E-07
X_{Pb}	0.011321	0.002387		0.002871

Reduction received in this calculation was 81.1% for particle matter. Since this calculation only differs from the previous case by having different calculation block and inflow stream values the overall findings are similar in this case.

3.3 Lumped model –tool

3.3.1 Overview and background of lumped modeling tool

As described before, user created higher fidelity calculation tools and existing modeling software were unable to model reduction behavior of heavy metals in a comprehensive manner. Wide range of heavy metals, reduction behavior, and their complex speciation create an ever-expanding modeling case. This leads to a very complex multispecies investigation filled with insufficient input data, calculation data, and behavior knowledge. These issues lead to the creation of the lumped modeling tool in this work. Lumped modeling can be used to greatly simplify modeling of complex phenomena influencing the investigated case. In general sense lumped modeling transforms distributed values into constants and adds the effect of different phenomena together in a *lumped* manner. For example, heat transfer of a wall can be simplified by using a constant wall temperature and overall heat transfer coefficient instead of a temperature distribution function and a combination of different heat transfer mechanisms, respectively. This approach to modeling makes complex systems easier to manage and these lumped parameters can be expanded and detailed through additional data and understanding of the system involved. This approach serves well the purpose of this thesis, as it can describe the overall behavior of heavy metal reduction in a comprehensive, albeit simplified manner and it has development potential to be expanded into a more distributed model. Instead of trying to calculate reduction by investigating the mechanisms described in subchapters 2.2.2 and 2.2.3, this calculation tool is based around reduction data gathered from multiple sources. Reduction data used consists of measurements of heavy metal concentrations before and after a scrubber or the heavy metal mass balance of the scrubber. This data can be used to calculate reduction coefficients that are used to simplify reduction

phenomena. Preliminary coefficients are received from data analysis in chapters 4 and 6.

Equations used in this tool are in two different groups: reduction and correction equations. Reduction equations are used to calculate heavy metal mass balance for the scrubber, calculate reduction itself, and ultimately produce concentrations in result streams. Correction equations are used to manipulate volume flowrates for gas and concentrations in gas flows. Equations 31-33 are so called reduction equations and 34-36 are used for corrections. Equation

$$\dot{m}_i = c_i \, \dot{V}_{gas} \tag{31}$$

where $\dot{m}_i$ [kg s^{-1}] is mass flowrate of a heavy metal species, c_i is heavy metal concentration in gas, and $\dot{V}_{gas}$ [m^3 s^{-1}] is inflow or outflow volume flowrate for gas. A similar equation can be used for condensate flowrate

$$\dot{m}_i = c_i \, \dot{V}_{condensate} \tag{32}$$

where $\dot{V}_{condensate}$ [l s^{-1}] is volume flowrate of condensate outflow, and c_i is heavy metal concentration in liquid. The actual reduction equation used is

$$\dot{m}_{i_{out}} = \dot{m}_{i_{in}} - k_{red_i} \, \dot{m}_{i_{in}} \tau_{res} \tag{33}$$

where $k_{red\ i}$ [-] is the reduction coefficient for a specific heavy metal and τ_{res} [-] is the dimensionless residence time used to correlate plant load. In this equation mass flows in and out are in gas flow and their difference is heavy metal mass flow in condensate. The correction equation

$$w_{cor} = \frac{100}{100 - x_{H_2O_{vol}}} \tag{34}$$

where w_{cor} [-] is a correction factor used to calculate species concentrations in dry flue gas and $x_{H_2O_{vol}}$ [-] is volume fraction of water vapor in wet gas. Equation

$$O_{cor} = \frac{20.9 - x_{O_2 ref}}{20.9 - x_{O_2}} \tag{35}$$

where O_{cor} [-] is a correction factor used to correct species concentrations to a set reference oxygen mole fraction. The term $x_{O2\ ref}$ [-] is reference mole fraction of oxygen in gas and x_{O2} [-] is the actual mole fraction. (EPA, 2016) Last equation is based on the ideal gas law.

$$NTP_{Cor} = \frac{T_{ref}\, p}{T\, p_{ref}} \tag{36}$$

where NTP_{cor} [-] is pressure and temperature correction factor, T and p are scrubber temperature and pressure, respectively. T_{ref} and p_{ref} are temperature and pressure in normal temperature and pressure (298.15 K and 1.01325 bar). (Zumdahl & DeCoste, 2013)

3.3.2 Tool creation and functionality

The creation of this tool is based around reduction coefficients and typical data available for scrubber design. In order to provide a comprehensive modeling tool, it has to be able to predict the reduction of most common heavy metals and produce usable results that can influence decisions in designing air control systems. Lumped calculations predict the reduction efficiency of particle matter and selected heavy metals, and also provide concentrations for heavy metals in outflow gas and wastewater. This tool is not influenced directly by heavy metal classification as it is already taken into consideration in reduction coefficients.

The tool is separated into two different portions: corrected and true species calculation. The tool is presented in Figure 13, where only corrected calculation is shown, but true species calculation has an identical layout.

Input

Fluegas inflow (wet)	50	(nm^3/s)	Gas moisture	8	vol-%	τ	1	
Fluegas outflow (wet)	40	(nm^3/s)	Oxygen content	9	mol-%	Pressure	1.01325	bar
Condensate outflow	10	(l/s)	Oxygen ref value	6	mol-%	Gas temperat	70	°C

Inflow gas (dry) O2 6 % (NTP)		Outflow gas (dry) O2 6 % (NTP)		Wastewater		Reduction
Components						
PM	70	22.7500	mg/nm^3	165.3481	mg/l	74
As	14	3.5000	$\mu g/nm^3$	35.7509	µg/l	80
Br	15	9.3750	$\mu g/nm^3$	23.9404	µg/l	50
Cd	53	17.2250	$\mu g/nm^3$	125.1921	µg/l	74
Co	25	9.3750	$\mu g/nm^3$	55.8608	µg/l	70
Cr	80	15.0000	$\mu g/nm^3$	217.0592	µg/l	85
Cu	200	50.0000	$\mu g/nm^3$	510.7276	µg/l	80
Hg	0.01	0.0044	$\mu g/nm^3$	0.0207	µg/l	65
Mo	45	8.4375	$\mu g/nm^3$	122.0958	µg/l	85
Ni	320	80.0000	$\mu g/nm^3$	817.1641	µg/l	80
Pb	200	55.0000	$\mu g/nm^3$	497.9594	µg/l	78
Sb	51	15.9375	$\mu g/nm^3$	122.0958	µg/l	75
Tl	76	19.0000	$\mu g/nm^3$	194.0765	µg/l	80
V	3	0.9750	$\mu g/nm^3$	7.0863	µg/l	74
Zn	150	48.7500	$\mu g/nm^3$	354.3173	µg/l	74

Figure 13: *Lumped model -tool interface (input and reduction values are placeholder)*

In true species calculation section input and output concentrations are actual concentrations present in gas or liquid flows. Corrected calculation portion handles input and output concentrations in a different way. Both input and output values are presented in a corrected form. This correction happens in three parts: moisture, oxygen, and NTP (normal temperature and pressure) correction. Moisture correction means that all gas flow concentrations are presented in dry gas. Oxygen correction is similar except con-

centrations presented are corrected for a reference oxygen mole fraction. Finally, NTP corrections means that gas flow volumes of are calculated in normal temperature and pressure: 298.15 K and 1.01325 bar.

The main input values of this calculation tool are wet flue gas inflow and outflow, condensate outflow, and most importantly particle matter and total heavy metal concentrations in inflow gas. Other input values deal with correction calculations such as inflow gas moisture, oxygen content, and scrubber temperature and pressure. There are also two additional input parameters: oxygen reference value and residence time τ. Main input values are used to calculate the heavy metal mass balance of the scrubber and other input values are used in concentration and gas flow corrections, excluding residence time. The term τ is used to estimate the deviation of residence time from its standard value of 1. This deviation is mainly caused by changes in power plant load. When used this parameter requires a user defined function to correct residence time into a dimensionless form, and also correlate residence time deviation to reduction efficiency.

As described previously, the reduction coefficients are received from measurement cases and data. Coefficients are typically reduction efficiencies received from aforementioned cases and data, and they can be changed freely while using this tool. The key idea in the functionality of this tool is to use the data from subchapters 4.2.3 and 6.3.4 to provide reliable reduction coefficients for a wide range of scrubber types, fuels, and boilers if available.

Correction factors in equations 34 and 35 can be used to convert true heavy metal concentrations in equations 31 and 32 into corrected forms by multiplying them. NTP_{cor} is used to convert true gas volume flowrate into volume flowrate in normal temperature and pressure. Calculations begin by using equation 31 and receiving heavy metal mass flowrates in to the scrubber. After these heavy metal mass flowrates for outflow streams are calculated with equation 33. Finally, heavy metal concentrations are calculated in both outflow gas and condensate using equation 31 and 32.

4. DATA SURVEY

This chapter is dedicated to gathering existing measurement data of heavy metal emissions. Data acquired from publications and previous measurement campaigns is collected and analyzed in the following two subchapters. First subchapter investigates heavy metal reduction of limestone scrubbers in coal-fired power plants and heavy metal emission streams, both flue gas and wastewater. The investigation has been divided into two parts: wastewater comparison and reduction efficiency comparison. Second subchapter is focused on data from previous measurement campaigns. Particular focus is on heavy metal reduction of caustic (NaOH) scrubbers in waste, SRF (solid recovered fuel), bio, and peat powered power plants. Reduction efficiencies presented in this chapter can be used in the lumped model –tool as reduction coefficients to improve its fidelity.

4.1 Data from publications

4.1.1 Overview of power plants and supporting data

This subchapter presents the necessary information and data supporting the actual measurement data. This information includes fuel data, flue gas pre-control, and other information considered important for the scope of this study. Support data can be used to help with result analysis and also provide a background for measurements in order create averaged reduction efficiencies.

Data used in wastewater comparison was retrieved from three publications and a total of 7 different measurement cases were analyzed. As described before, all of the plants have wet limestone scrubbers and are typically large power plants excluding one (plant ID: Ohki A1 and C1), which consist of measurements made in a coal-fired pilot plant. Data used in reduction efficiency measurement cases is also from coal power plants with limestone scrubbers, but data presented is typically averaged from various power plants and publications. Additional supporting data of these power plants has been listed in Table 11. Usually detailed information on fuel consumption and plant operating parameters were not specified, but some information is available that can give some perspective. The average lower heating value of coal in measurement cases examined in (Tang, et al., 2012) is 20 [MJ kg^{-1}] and all power plants examined were 600 MW excluding Luohi 2, which is 300 MW. Cordoba provided a fuel feed in rate of 143 and 152 [t h^{-1}] for measurement cases, and in the pilot plant used in (Ohki, et al., 2011) had a fuel feed rate of 100…120 [kg h^{-1}]. (Cordoba, et al., 2012; Ohki, et al., 2011; Tang, et al., 2012)

Table 11: *Supporting data for measurements cases used in wastewater comparison* (Cordoba, et al., 2012; Ohki, et al., 2011; Tang, et al., 2012)

	Luohe 2	Luohe 3	Pingwei 1	Pingwei 2	Ohki A1	Ohki C1	Cordoba 1	Cordoba 2
Pre-control	ESP	ESP	ESP	ESP	SCR + ESP	SCR + ESP	ESP	ESP
Fuel	Coal	Coal	Coal	Coal	Coal	Coal	Petcoke and coal mix	Petcoke and coal mix
Approximate fuel feed in rate [kg s^{-1}]	40	80	80	80	0.03	0.03	40	40

Other measurement cases and data used contains mean values, thus a specified supporting data is not available. ESP stands for electrostatic precipitator, SCR stands for selective catalytic reduction, and petcoke refers to petroleum coke. Knowing flue gas pre-control systems is vital, because they can for example, reduce particle emissions and oxidize heavy metal compounds.

4.1.2 Measurement data analysis

First, the measurement results are presented and after that they are analyzed. Results have been chosen mainly based on availability, but also by their usefulness in finding reduction coefficients for lumped model –tool. Discussion (chapter 6.2) is present to describe problems in this regard. Reduction efficiencies are listed in Tables 12 and 13 and some data regarding heavy metal concentrations in fuel and water flows can be found in Figures 14 – 16.

Table 12: *Reduction efficiencies for arsenic (As) and different mercury (Hg) species* (Cordoba, et al., 2012; Tang, et al., 2012; Tian, et al., 2010)

Element	Cordoba 1	Cordoba 2	Tian WFGD	Wet scrubber	Luohe 2	Luohe 2	Pingwei 1	Pingwei 2
As	67-92	91-98	80.38	96.3	75	100	50	65
Hg_{tot}	65	21	57.22	15.15	82	82	80	80
Hg^{2+}	74	24						
Hg^{0}	17	9.1						

Reduction efficiencies shown in Table 12 for Cordoba are gaseous emissions and in Table 13 they are particle emissions. Overall particle reduction in wet scrubber was 46 – 92% in Cordoba 1 and 65 – 91% in Cordoba 2. It is also discussed that most heavy metals had low volatile behavior and were not present in gas phase after leaving boiler. Arsenic behavior was the only heavy metal in (Cordoba, et al., 2012) to have class II be-

havior, but only 2% remain in gaseous phase and 98% is found in fly ash. Mercury had typical class III behavior but there was also a great deal of re-emission through entrainment of scrubbing liquid. Due to changes in particle reduction in electrostatic precipitator between Cordoba 1 and 2 measurement cases are produce fairly different reduction efficiencies. (Cordoba, et al., 2012)

Table 13: *Reduction efficiencies for various heavy metals* (Cordoba, et al., 2012; Tian, et al., 2014; Cordoba, 2013)

Element	Cordoba 1	Cordoba 2	Cordoba mean	Tian 2014
Arsenic (As)	42.86	45.00	70.89	80.38
Bromine (Br)				
Cadmium (Cd)	50.00	0.00	-50	80.5
Cobalt (Co)	76.19	66.67	78.95	
Chromium (Cr)	98.79	56.41	40	86
Copper (Cu)	86.49	55.56	24.56	
Molybdenum (Mo)	66.92	99.95	51.52	
Nickel (Ni)	95.18	52.31	68.89	80
Lead (Pb)	72.38	68.42	80.95	78.4
Antimony (Sb)	58.82	69.23	75	82.1
Thallium (Tl)	42.86	80.00	50	
Vanadium (V)	59.40	70.27	81.92	
Zinc (Zn)	29.09	52.50	71.38	

In cases Cordoba 1 and 2 all other heavy metals in flue gas, excluding arsenic and mercury, were completely found in fly ash. Also, arsenic was found to be 98% in fly ash, so when determining reduction, it is assumed to be solely found in fly ash. By comparing reduction rates for these heavy metals with particle matter removal, some estimates can be made. This method assumes that all heavy metal condensing happens on existing particles and no homogenous nucleation takes place. Then by comparing reduction efficiencies of heavy metals with their inflow concentrations in particle matter, it can be determined whether heavy metal inflow concentration is too small to provide accurate reduction efficiency. This observation eliminates Cordoba 1 reduction rates of As, Cd, Mo, Sb, and Tl. For Cordoba 2 As, Cd, Co, Cr, Cu, Ni, Pb, and Tl are eliminated. A similar investigation is performed for very high reduction rates in order to determine whether they are inconsistently inflated by the inflow concentration. Now that some reduction efficiencies have been eliminated remaining efficiencies are compared with rates presented in (Tian, et al., 2014) and particle reduction in Cordoba cases.

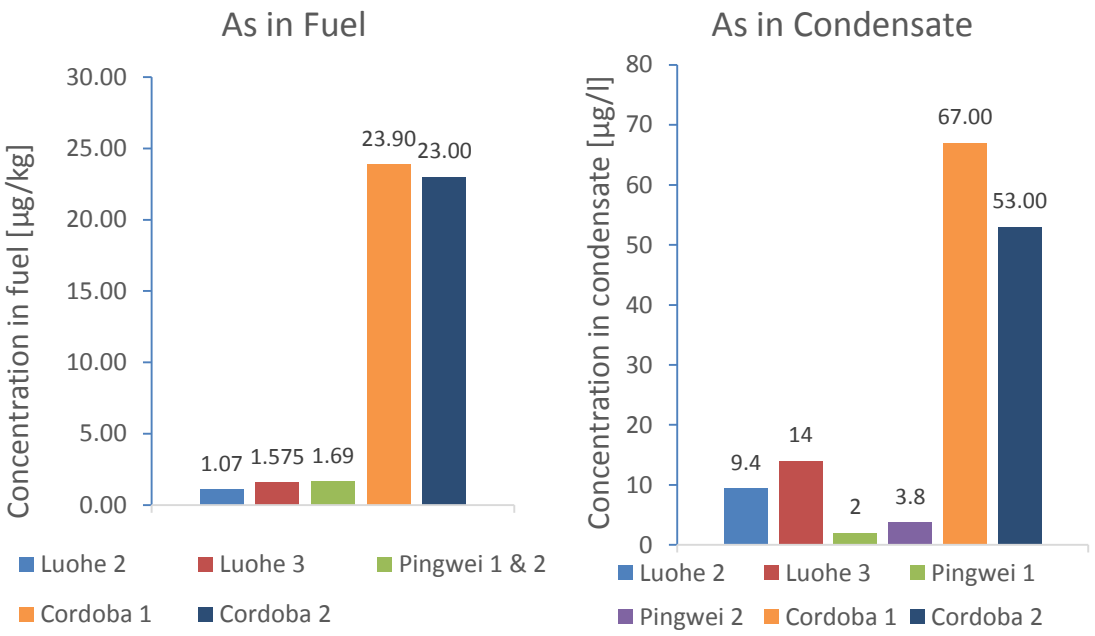

Figure 14: *Arsenic in fuel and condensate* (Cordoba, et al., 2012; Tang, et al., 2012)

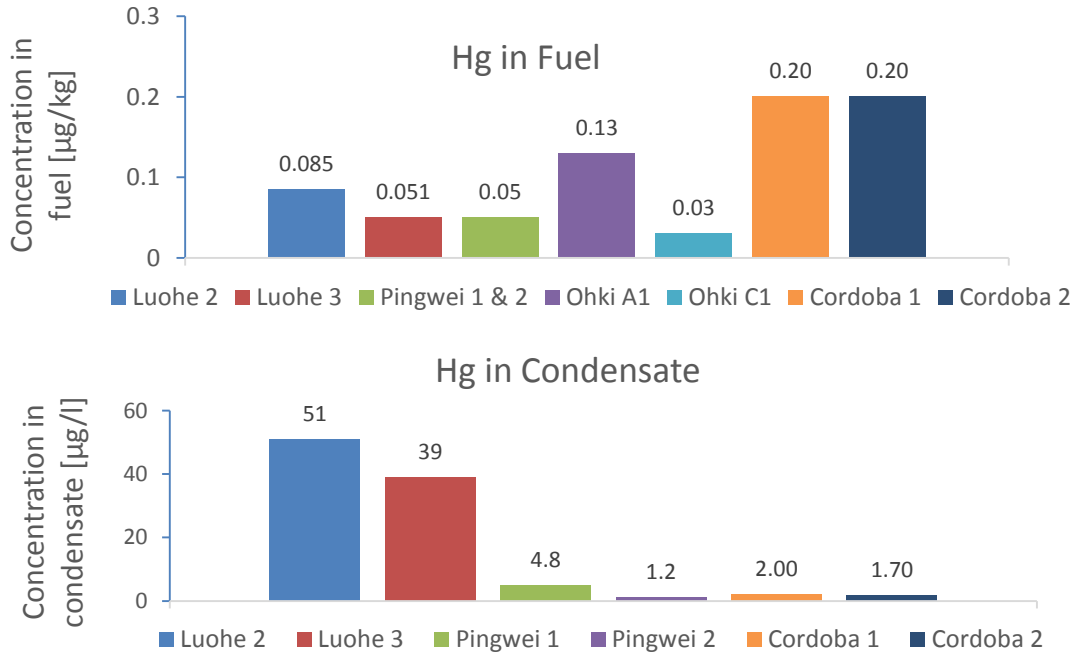

Figure 15: *Mercury in fuel and condensate* (Cordoba, et al., 2012; Ohki, et al., 2011; Tang, et al., 2012)

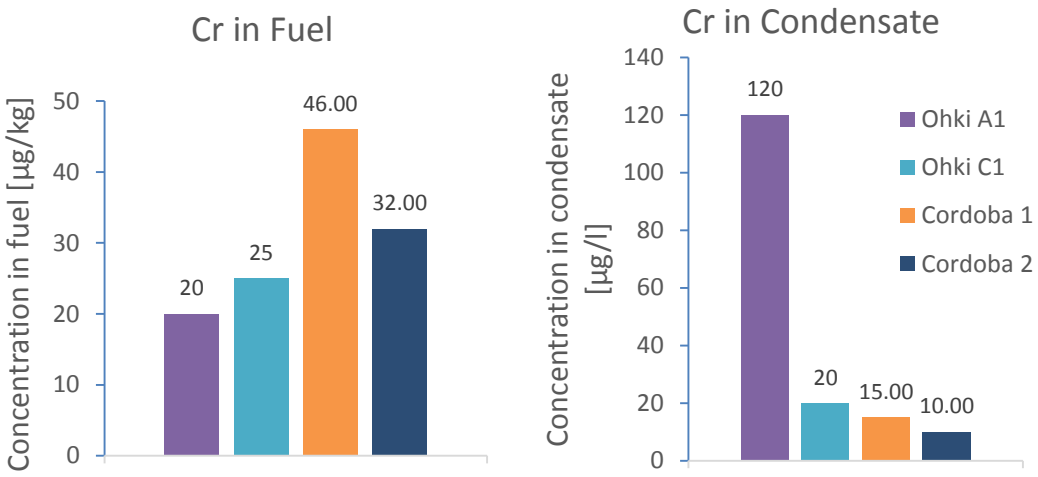

Figure 16: *Chromium in fuel and condensate* (Cordoba, et al., 2012; Ohki, et al., 2011)

Cordoba 1 and 2 mercury in condensate was labeled as [mg l^{-1}] instead of [µg l^{-1}] as everything else. It was added to Figure 16 as [µg l^{-1}]. Description of fuel and condensate heavy metal analysis was easier to do as data availability was better, but on the other hand this data cannot be used alone to calculate reduction efficiencies without better supporting data. Supporting data would need to contain flue gas and condensate volume flowrates, partitioning factors between flue gas and bottom ash, and also reduction involving pre-control devices such as ESP. No conclusions can be drawn based on data in Figures 14, 15, and 16, due to no correlation behavior observed between power plants or measurement cases. A basic overview of plant parameter influence on reduction could have been investigated, if some correlations would have emerged. Any credible analysis based on fuel and water heavy metal concentrations is not feasible with data available as there a simply too many variables and not enough data points. Figures 14, 15, and 16 can act as examples for typical values that can be found in solid fossil fuels and limestone scrubber wastewater.

A set of average reduction efficiencies is presented in Table 14, but their fidelity and applicability is highly questionable and they should only be used as general approximates. Mercury reduction is highly dependent on its speciation and its reduction rate has been described as a range. If no useful data was available, average particle removal efficiency received from (Cordoba, et al., 2012) was used. These values have been marked with a ”*” symbol.

Table 14: *General approximations of heavy metal reduction received from data analysis of this subchapter*

Element	Arsenic (As)	Cadmium (Cd)	Cobalt (Co)	Chromium (Cr)	Copper (Cu)	Mercury (Hg)	
Reduction efficiency	0.75	0.80	0.775	0.86	0.80	0.2 - 0.6	
Element	Molybdenum (Mo)	Nickel (Ni)	Lead (Pb)	Antimony (Sb)	Thallium (Tl)	Vanadium (V)	Zinc (Zn)
Reduction efficiency	0.74 *	0.80	0.784	0.785	0.74 *	0.74 *	

4.2 Previous measurement data

4.2.1 Overview of power plants and supporting data

This subchapter is dedicated to presenting the general information of the power plants investigated in previously conducted measurements. In this investigation a more comprehensive approach was taken due to better data availability. Investigation focused only on determining reduction efficiencies for heavy metals, but did this in a more detailed manner. This data survey consists of measurements performed in 6 different power plants (Plant ID: 1 – 6) and has 13 measurement cases. Power plants were selected based on their boiler type and also focusing on bio and recycled fuels. These plants typically had bubbling fluidized bed (BFB) boilers, excluding plants 5 and 6 which had power boilers. Power plants were also classified into 3 different groups: power boiler group, BFB with waste combustion and without waste combustion. Lower heating value was not presented in all the measurement cases but in plants 2 and 3 mean LHV was between 9.5 – 10.5 [MJ kg^{-1}]. Lower heating values were specified for peat and bio fuel in plant 2, plant 3 LHV was defined for sludge and reject. Almost all of the plants had the same scrubber type, expect plant 4. General scrubber type was a two section scrubber, where the first section consists of a countercurrent spray tower and the second section has a packed-bed scrubber. Plant 4 only has a packed-bed scrubber similar to the second section in previous cases. Table 15 contains supporting data that varies between plants, such as power, fuel type and pre-control devices. (Valmet, 2016)

Table 15: *Supporting data for previous measurement plants* (Valmet, 2016)

Plant ID	1	2	3	4	5	6
Power [MW]	170	70	37	100	10	2*5
Fuel	Peat, SRF	Peat, Bio	Sludge, Reject, Gas	Bark	Peat	Bark, Wood
Pre-control	ESP	ESP	SNCR, FF	-	-	-

SRF stands for solid recycled fuel, SNCR for selective non-catalytic reduction, and FF for fabric filter.

4.2.2 Measurement data analysis

Due to a greater availability of more detailed data than in public survey, a more comprehensive approach to heavy metal reduction efficiency was taken by attempting to calculate actual mass flow rates for heavy metals entering the scrubber in flue gas and exiting it in flue gas and condensate. With this information it would have been possible to calculate reduction values of both sections of the scrubber and also confirm the accuracy of the measurement case by calculating mass balance differences for each heavy metal. Unfortunately, due to great deficiencies in supporting data and the lack of condensate samples made this approach impossible. In addition, to confirm heavy metal measurements and heavy metal speciation between bottom and fly ash, heavy metal analysis of fuel samples could have been useful but was also systematically lacking.

Despite deficiencies in support and measurement data, a more comprehensive reduction efficiency evaluation in comparison to public data was made. This was achieved by having more measurement cases, support data to help compare and validate results, and more detailed heavy metal measurements from flue gas. In some measurement cases heavy metal concentrations in gas were reported both in particle and gas phase, which helped both results and speciation analysis. According to (Maunula, et al., 2016) gas phase measurements cannot differentiate between gaseous molecules and aerosols. Using this knowledge, it is assumed that only class III heavy metals are in gaseous phase and rest are aerosols or small particles in gas phase measurements.

By using data presented in Figures 17 – 20 the accuracy, comparability, and correlation of measurement cases and their differences can be estimated. In plant 2 a, b, and c represent different measurement cases using biofuel, peat, and mixture of those two, respectively. First an overview of the accuracy and confidence of the measurement data is evaluated through a qualitative process. Second, focusing on Figure 17 and the reduction rates achieved in this histogram, the dependence on reduction and plant parameters was examined. Finally, the effect of gas proportion and heavy metal inflow concentration is discussed.

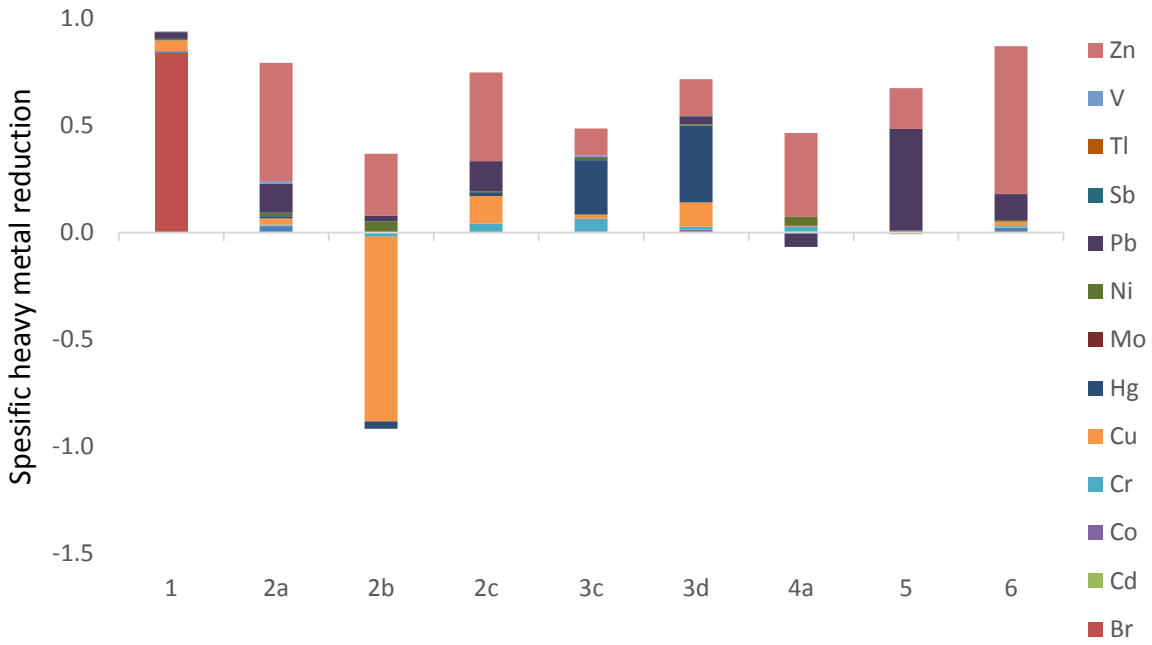

Figure 17: *Total and specific heavy metal reduction (x-axis values are power plant IDs)*

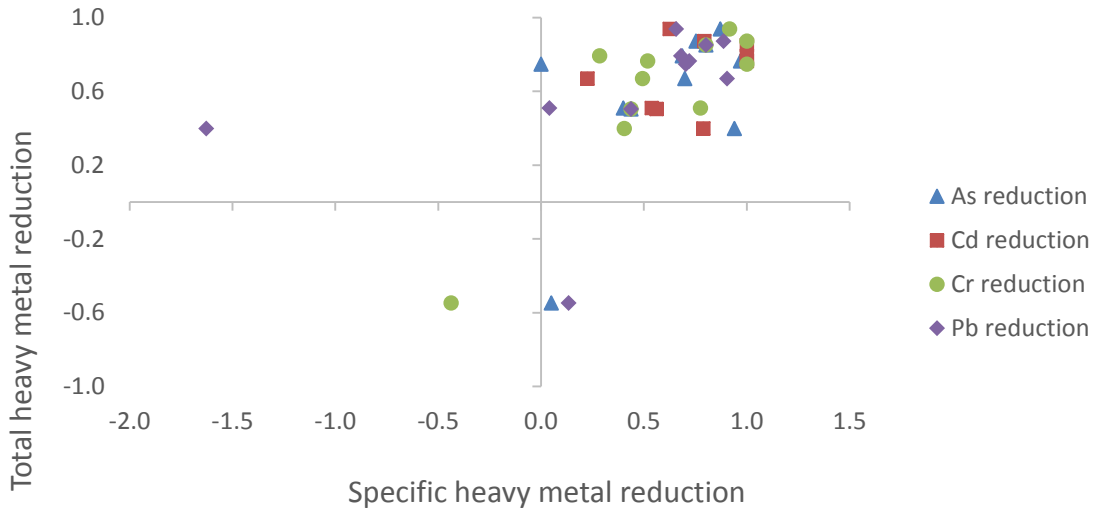

Figure 18: *Total and specific heavy metal reduction correlation graph*

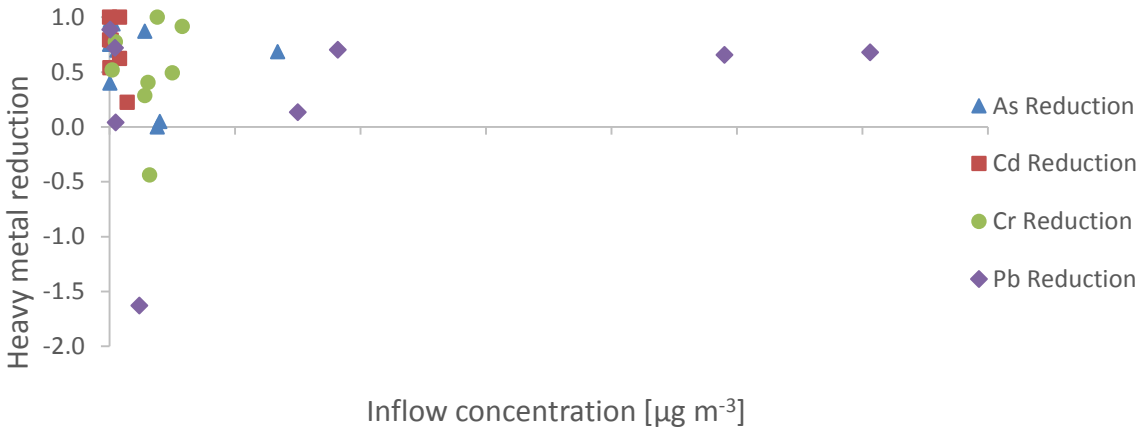

Figure 19: *Specific heavy metal reduction and inflow heavy metal concentration correlation graph*

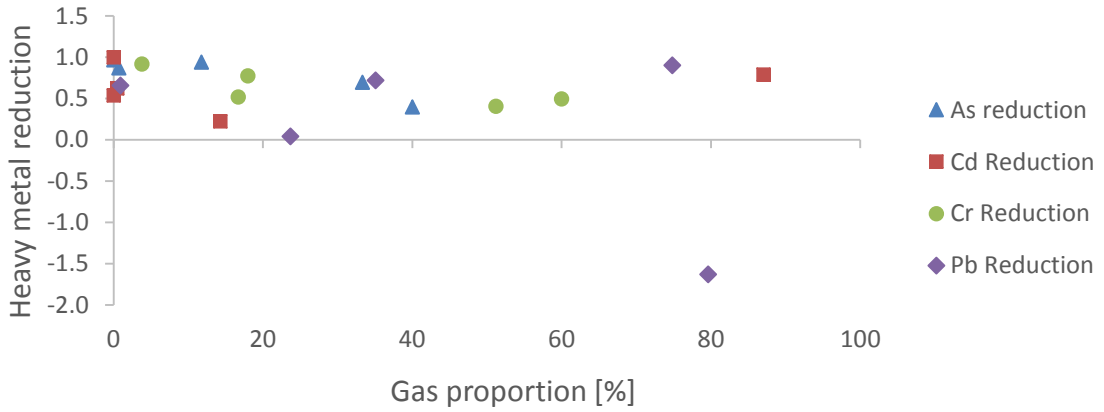

Figure 20: *Specific heavy metal reduction and gas proportion correlation graph*

First by observing the overall view of these figures, it becomes clear that no clear correlations emerge. It should be noted that only certain class II metals were chosen to be compared in these figures in order to reduce factors, since it is presumed that these heavy metals share a similar behavior. Figures 18 – 20 scatter series seem random and uncorrelated by change in the x-axis parameter (Figures 18 and 19) or y-axis (Figure 20). In every case and heavy metal type, the specific reduction values fail to form any type of correlation. When comparing specific scatter shapes formed in these figures, it becomes quite clear that all heavy metals compared behave in an inconsistent matter. Also no group behavior was determined for boiler, pre-control, or fuel type. This is most likely caused by a lack of similar power plants. Also the expected inaccuracies in measurements methods and calculations cause issues with fidelity.

By observing Figure 17 some interesting findings can be acquired. For example, the large reduction rate of bromine in plant 1, which was not measured in other plants. Also

the significance of zinc reduction present in many cases. A high zinc reduction seems to be present in power plants using bio fuels, especially wood and bark. It also seems to be present regardless of boiler type and pre-control, since it can be observed in cases 2a, 2c, 4 and 6. Also a slight change in zinc reduction when comparing 2a and 2c can be observed. Comparisons between power plants 1 and 3 can be made but it is muddled due to different pre-control systems and also the vague definition of SRF used in plant 1. Ignoring the large bromine reduction in plant 1 and comparing the remaining values with plant 3, it can be seen that plant 3 has very significant mercury reduction efficiencies in comparison. Plant 1 has large lead and copper reduction rates that are not represented in a similar proportion plant 3 cases.

The very large mercury reduction in plant 3 is puzzling and cannot be explained by theoretical behavior described in chapter 2. Because pre-control devices have no significant interactions with mercury, the great reduction efficiency of Hg in general, and in comparison to other reduction rates found in plant 3 cases indicate two possibilities: active carbon system or large measurement errors. Active carbon can be used to adsorb gaseous mercury and greatly increase its reduction. This should have been present in support data. Another cause can be the large measurement errors, due to small inflow concentrations. This discrepancy could also be caused by the large difference in plant power but determining this effect would require more measurement cases. In plant 5, a large lead reduction is observed but it cannot be compared with other cases easily, due to plant parameter differences. Although a somewhat large lead reduction rate is present in plant 1, differences are too great to make any sort of confident assumption. In lesser extent, reduction rates of cadmium, chromium, and copper seem to be more significant in BFB boilers, but drawing any concrete conclusions are ill advised.

In Figures 18 – 20 specific reduction values increase and decrease while moving in one direction on the opposing axis. This indicates that specific reduction is not influenced by inflow concentration and gas proportion, although this should not be the case. A higher inflow concentration should be easier to measure and reduction rate should be more clearly noticed. But in the figures reduction rates fluctuate and at very high concentrations remain similar. For example, by observing lead reduction it should be seen that smaller inflow concentrations produce smaller reduction rates due to measurement limits and inaccuracies, but instead largest reduction rates are found at the lowest concentrations. This fluctuation could also be affected by differences in power plant parameters and devices, but due to lack of measurement cases this cannot be confirmed.

As described in the previous subchapter, gas measurements can also contain aerosol particles, which supports the idea of class II heavy metal behavior observed in Figure 20. Relying on finding in (Cordoba, et al., 2012) and chapter 2.1 on class II heavy metal behavior it is assumed that As, Cd, Cr, and Pb fully condensate on particle matter before the scrubber. This would mean that as the gas proportion increases, more heavy metals are contained on submicron and aerosol particles. Scrubbers cannot collect

smaller particles as effectively and there should be a very clear decrease in specific heavy metal reduction as gas proportion increases. This correlation is not present in these measurement cases as can be seen in Figure 20. A minor behavior similarity can be observed in Figure 18, where total heavy metal reduction efficiency is between 0.8 and 1 all specific heavy metal reduction rates are between 0.6 and 1. This is an interesting finding since below this limit specific reduction values range from 0 to 0.9. This indicates that when total heavy metal reduction rates are high enough, specific reduction rates also produce a more focused cluster. This behavior will be examined further using data from measurement campaigns. In addition, particle and heavy metal reduction rates were briefly compared in order to determine a positive correlation between class I & II heavy metal and particle reduction. Data for such an investigation was unavailable. By using data from appendix A1 it can be determined that particle reduction rates were usually high, but did not seem to correlate well with class I & II heavy metal reduction, or the measurement accuracy (i.e. negative reduction rates or detection limits used calculated reduction rates).

Finally, an observation into heavy metal speciation can be performed with appendix A2, where gas proportions of heavy metal measurements are reported. Basing expectations on heavy metal gas proportions on classifications defined in chapter 2.1, cobalt should always have a very low gas proportion, all other heavy metals excluding mercury and bromine should also have lower percentages. Mercury on the other hand should have very high gas proportion. First by observing the mercury proportions, it can be concluded that its behavior seems to match well with theoretical knowledge, as gas proportions are high and are increased while going through the scrubber. This increase in gas proportions supports the idea of elemental mercury insolubility and particle bound mercury reduction through particle capture mechanisms. Other heavy metals have less reliable behavior patterns, since in some cases gas proportions seems the decrease in scrubber, which is not expected, due to heavy metal reduction being tied to particle reduction. A decrease in gas proportions indicates that smaller particles were captured more easily in the scrubber, or that these heavy metals were in gaseous form, which is not supported by theoretical understanding. For example, in plant 5 copper goes from 100% to 39% gas proportions, which is strange behavior and indicative of issues in measurement accuracies. By observing changes in gas proportions, the data may be used to find measurement inaccuracies that might be overlooked while only observing total reduction efficiencies.

4.2.3 Reduction efficiency analysis

In the previous subchapter reduction coefficients for lumped model –tool were defined and reported. This will also be conducted here, but since there was more data available and confidence in measurements is higher, there are multiple pathways to determine reduction coefficients: average, novel approach (similar to public survey approach), and

a new and improved novel approach. Table 16 contains the reduction coefficients acquired from previous measurement data. Average reduction coefficient is calculated by using appendix A1 reduction rates, but negative values are left outside the average. Novel 1 idea calculates averages without using very small reduction efficiencies (<0.1). Finally, Novel 2 idea is based on Novel 1 but is expanded by excluding reduction rates calculated with values at or under detection limit.

Table 16: *Reduction coefficients acquired from previous measurement data*

Filtering method	Particle matter (PM)	Arsenic (As)	Bromine (Br)	Cadmium (Cd)	Cobalt (Co)	Chromium (Cr)	Copper (Cu)	Mercury (Hg)
Average	0.815	0.509	0.982	0.726	0.702	0.579	0.270	0.473
Novel 1	-	0.575	-	0.726	0.702	0.658	0.517	0.654
Novel 2	-	0.544	-	0.726	0.695	0.649	0.547	0.671
Filtering method	Molybdenum (Mo)	Nickel (Ni)	Lead (Pb)	Antimony (Sb)	Thallium (Tl)	Vanadium (V)	Zinc (Zn)	total
Average	-	0.670	0.597	0.460	0.689	0.861	0.710	0.646
Novel 1	-	0.718	0.597	0.460	0.580	0.861	0.710	0.676
Novel 2	-	0.698	0.658	-	0.756	0.833	0.710	0.717

It is possible to use these values as reduction coefficients in lumped model –tool, however certain precautions have to be stated. These values are based on heavy metal measurement data that can be unreliable even in the best cases. A great number of factors, such as measurement inaccuracies caused by low heavy metal concentrations, detection limits, and effective particle pre-control, affects reduction coefficients. Since no grouping behavior was determined for the different kind of power plants, these values are calculated by using all measurement cases. These values have to be validated by using other measurement data and comparing the results to lumped model –tool calculations. When choosing the type of values to use in lumped model –tool, there are only two real options. Average reduction rates should not be used at all, since they are only a very rough estimate. By investigating changes in values it can be determined, how much the data filtration affects the heavy metal reduction rate. Greater the change, poorer are the overall measurement results in general. The more fluctuation found in these values, the more likely they have inaccuracies.

Another value to compare the results with is the total reduction rate. By using a combination of fluctuation and total reduction comparison some heavy metals stand out as problematic: copper, antimony, and to a lesser extent arsenic. Copper has low reduction values and great fluctuation, antimony on the other hand has little fluctuation, but its Novel 2 approach cannot be calculated due to poor measurement values. Arsenic is not

suffering from fluctuation but produces low reduction rates. Also by comparing class I & II heavy metal reduction values, similarities should arise, if measurement data is accurate. All heavy metals excluding class III seem to have similar reduction values. Although chromium, lead, and vanadium stand out by having slightly lower or fairly higher values. Using Novel 1 or 2 values is recommended, since poor values have been removed from their average calculations. Novel 1 values are more conservative, but also have more data points in averaging calculations. Novel 2 on the other hand produces uses more accurate data but less data points. It can be hard to determine which values to use and rigorous future testing is required.

5. MEASUREMENT CAMPAIGN

This chapter is dedicated to the measurement campaign conducted during thesis work. The purpose of these measurements is to provide additional measurement data to investigate further the reduction phenomena, previous measurement data accuracy, and improve measurement and data analysis confidence through more rigorous data collection. As was shown in the data survey chapter, measurement data is not available in a great supply, thus additional well-documented measurements are always useful. These measurement results are evaluated by a similar process as was conducted in the previous chapter to determine general similarities. Finally in chapter 6.3, an improved data analysis is performed on the data to determine, whether it provides any useful information.

5.1 Campaign overview

5.1.1 General measurement plan

This general measurement plan describes the overall idea and execution of the measurement campaign. It is used to draft more detailed plans for power plants selected and can be modified if needed to fit the realities during measurements, but the baseline approach is to do every measurement according to this plan. This guarantees two things: every scrubber is investigated in a similar and comprehensive manner and that measurements conducted in the selected power plants are comparable.

The measurement plan is drafted on a power plant scale, i.e. it covers the measurements conducted in one power plant. The measurements are divided into cases, and each set of measurements performed at any power plant contains two cases. These cases are identical in all ways except one, a change in wet scrubber operating parameter. This parameter in all measurements is pH, which is controlled by scrubbing chemical (NaOH) feeding into the scrubbing liquid. The measurements in one case include heavy metal concentration measurements in both flue gas and scrubbing liquid, supporting data such as oxygen mole-fraction and moisture in flue gas, flue gas volume flowrate, plant operating parameters, and as an optional addition, particle matter concentrations in flue gas. Heavy metal concentrations in flue gas are measured in both particle and gaseous phase. It has to be noted that submicron and aerosol particles can be found in the gaseous phase (upper limit values range from 0.3 – 1.2 μm (Maunula, et al., 2016)). These measurements are gathered in a single, long collection sample lasting the entire case timeframe. Heavy metal samples taken from used scrubbing liquid, i.e. condensate can be taken very quickly, thus more than one can be taken during the measurement case.

Since they can be taken so quickly, this measurement location can be used to investigate the effect of uncontrollable changes power plant operating parameters, and their influence on heavy metal reduction. Additional samples will only be taken if unscheduled events take place in the power plant. These events can be for example, device malfunctions or uncharacteristic combustion behavior. Heavy metal samples from the flue gas are taken before the scrubber and in the stack. Heavy metal concentrations in used scrubbing liquid are only measured as it is circulated in the system and the expected change is too small to measure. In (Liikanen, 2016) it was expressed that in order to support the heavy metal measurement data, the flue gas state, moisture and oxygen content has to be known. These values are measured by using continuous measurement methods.

In addition to the support measurements, operating parameter data is collected by the automation system used to manage the power plant. Optional measurements include particle matter concentration in flue gas. Taking these particle samples is limited by the availability of measurement couplings. If there are more than one coupling before and after the scrubber, then it is possible to take particle samples. Otherwise these samples would be taken outside of case measurement timeframe. The measurements in each case are compiled into Table 17. This Table contains the location, sampling method, and measurement standard for all the measurements performed in one measurement case. Mercury and other heavy metals are separated in the Table, due to their behavioral differences, which leads to different measurement methods.

Table 17: *The measurements performed in flue gas during a single measurement case* (Liikanen, 2016)

Heavy metal measurements:			
	Measurement location	Continuous / sample	Standard
As, Br, Cd, Co, Cr, Cu, Mo, Ni, Pb, Tl, Sb, V, Zn	Flue gas: before and after scrubber Condensate: outflow	single sample (flue gas) single/multiple samples (condensate)	SFS-EN 14385 (flue gas) SFS-EN 1911 (Br)
Hg	Flue gas: before and after scrubber Condensate: outflow	single sample (flue gas) single/multiple samples (condensate)	SFS-EN 13211 (flue gas)
Support data measurements:			
O_2	before and after scrubber	continuous	
Moisture	before and after scrubber	continuous	SFS-EN 14790
Volume flow	before and after scrubber	continuous	SFS-EN 16911-1
Power plant operating parameters	various	continuous	

Figure 21 presents the layout of a condensing scrubber and measurement locations for heavy metals.

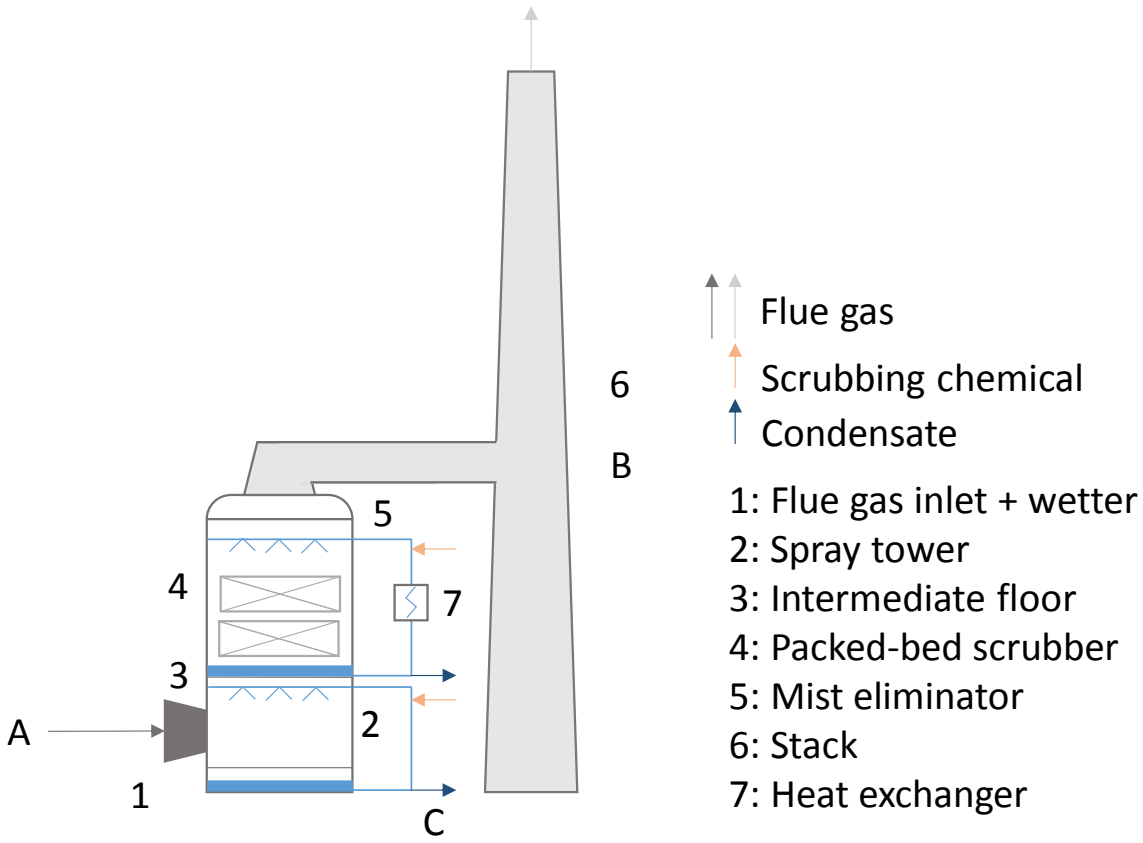

Figure 21: *Layout and measurement points of a two-stage caustic wet scrubber*

Figure 21 describes locations of the measurements conducted in each case. They are labeled as A, B, and C: before scrubber, stack, and condensate, respectively. Locations A and B are used for flue gas measurements and sampling. Measurement point A is located before the flue gas inlet and wetter, in the flue gas duct. Point B is located in the stack, after the mist eliminator. Heavy metal sample taken from used scrubbing liquid, known as point C. Point C is not as straightforward as points A and B, because some scrubber layouts can contain two condensate outflows. Heavy metal samples are taken from the liquid circulation or the condensation outflow pipe. If there are two condensate outflow locations (upper and lower), both scrubbing liquid circulations are sampled. In the case of only one outflow pipe, only that circulation is sampled. In Figure 21 there are two outflows: upper and lower. The general idea is to take a sample representing heavy metal concentration in condensate outflow. Because the change in heavy metal concentration in scrubbing liquid before and after scrubbing is extremely small, heavy metal concentrations are only measured to examine condensate outflow.

5.1.2 General analysis plan

In addition to a measurement plan, an organized analysis is also required to handle the received results in a useful and similar manner. Together with the general measurement plan, both measurement practices and analysis can be streamlined for all measured power plants. A pre-planned analysis can also help with prioritizing measurements under fiscal or time constraints.

The data analysis is divided in to two parts: plant specific analysis and a comparative analysis. The first part is conducted to evaluate the accuracy of the measurements, behavior and reduction of heavy metals in a detailed manner. Comparative analysis is used to find similarities in evaluations performed in power plant specific analysis. Comparisons are used to determine repeating measurement inaccuracies, similar reduction and class behavior, and also the impact of power plant design parameters, such as fuel, precontrol, or boiler type.

Plant specific analysis is mainly based around the idea of calculating a heavy metal mass balance for the wet scrubber. Two other investigation methods are used, comparison of reduction efficiency and gas proportion for heavy metals. Since two cases are conducted in each power plant with different scrubbing liquid pH, a comparison can be drawn between these cases. This comparison is used to find pH dependent reduction efficiencies and to determine theoretical behavior. Heavy metal mass balance in the wet scrubber is calculated by determining inflow and outflow mass flow rates for every heavy metal. Inflow rate consists of incoming flue gas and is calculated with heavy metal concentrations and flue gas volume flow rate. All calculations involving flue gas have to be performed with similar values, i.e. wet and true flowrate and true concentrations in wet gas, or dry and NTP corrected flowrate and dry, oxygen corrected concentrations. Outflow heavy metal mass flow rates are a sum of heavy metals in outflow flue gas and condensate flows. Heavy metal mass flow in outflow flue gas is calculated in a similar way as inflow. Heavy metal mass flow in condensate flow(s) are calculated by using condensate volume flow rates acquired from power plant operating parameter data and heavy metal concentrations in used scrubbing liquid. Heavy metal mass flow rates in flue gas are then used to calculate reduction efficiency. By using inflow and outflow heavy metal flow rates, a mass balance can be investigated. This means that inflow and outflow streams should be equal and discrepancies are solely caused by measurement inaccuracies or changes in power plant operations.

Heavy metal classification behavior can be investigated by comparing reduction efficiencies of mainly class II heavy metals. Large differences can indicate measurement errors, since their behavior is expected to be similar. There should also be a negative correlation between gas proportion and heavy metal reduction, particularly for class II heavy metals. If particle matter measurements are available, an evaluation of class I & II heavy metal and particle reduction can help to determine speciation behavior of heavy

metals. As an example, higher gas proportions should indicate lower reduction efficiencies for class I & II heavy metals and even a small gas proportion is expected to lead to a reduction efficiency lower than particle reduction. This is caused by the systematic error in measurements, which causes very small particles to be mistakenly added to gas phase concentration. These aerosol and submicron particles are difficult to capture in a wet scrubber, thus causing a lower reduction efficiency.

Comparative analysis is performed for two purposes: to evaluate the comparability of different power plant measurements and to determine overall reduction efficiencies. When investigating comparability, analysis is based on a qualitative approach to find similarities in all cases or instead trying to find behavioral groups. These behavioral groups are similar to groups proposed in chapter 4.2, for example grouping by boiler or scrubber type. These figures are drawn in a way that correlates reduction efficiencies and other heavy metal measurement values, such as inflow concentrations, gas proportions, and total heavy metal or particle reduction efficiency. Scatter figures produce shapes that can easily be investigated whether grouping behavior exists and if behavior is relatively similar in all cases, unaffected by power plant design parameters. Histograms are drawn in order to investigate differences in heavy metal type reduction between cases. Here correlations between boiler or fuel type can be found if they exist. Otherwise they are used to the same goal as scatter figures. This approach can be used to examine clear differences in reduction behavior, but also to estimate the accuracy of the measurement campaign by comparing findings with theoretical knowledge.

The other purpose of comparative analysis is to produce a set of reliable reduction efficiencies that can be used in the lumped model –tool as reduction coefficients. This analysis is performed for every group found or for every case investigated, if results prove to be comparable. Similar approach to reduction efficiency evaluation is used as in chapter 4. First reduction rates are averaged, after that data is filtered and measurements of poor value are removed. Poor values can be formed by measurement inaccuracies, low concentrations, and detection limits. After multiple filtering passes, average reduction efficiencies are formulated. Filtering passes include the removal of negative and near-zero reduction values, extremely high and low concentration values, any measurement values very near to detection limit, and large deviations from expected mass balance values. By investigating the change in reduction efficiencies between filtering passes, the quality of the measurement campaign in general can be estimated. The greater the fluctuation, more values are affected by the filtering, thus lowering the number of data points.

5.2 Power plant overview and deviations from the general plan

5.2.1 Power Plant T

In subchapters 5.2.1 and 5.2.2, the basic power plant and environmental system information and supporting plant data is presented. These subchapters also contain any deviations from the measurement plan discussed in 5.1.1. This power plant information is used to try and find clear similarities or differences between the following two power plants and previous measurement data regarding heavy metal speciation and reduction.

Power plant T is a waste combustion CHP (combined heat and power) plant located near a municipal waste handling center. Its primary fuel is municipal waste, which is combusted in a grate type boiler. This waste fuel consists of mixed and energy waste, thus it can have inconsistent physical and combustion properties, especially lower heating value. Environmental systems in this power plant consists of electrostatic precipitator, semi-dry scrubber consisting of calcium compound and active carbon feed-in systems, fabric filter, and a two-stage condensing wet scrubber. First stage in the wet scrubber is a spray tower, and the second stage is a packed-bed scrubber. Since power plant T is a waste combustion facility, rigorous flue gas control systems are required to comply with emission regulations. Power plant T information has been compiled into Table 18. (Maunula, et al., 2016; Valmet, 2016)

Table 18: *Power plant T basic and environmental system information* (Valmet, 2016)

Boiler	Power [MW]	Pre-control	Wet scrubber	Fuel	LHV [MJ kg^{-1}]	Cases
Grate	58	ESP, semi-dry-scrubbing, FF	Two-stage: Spray tower, packed-bed	Municipal waste	highly varied	T1

Due to such rigorous flue gas control systems, the amount of particles reaching the wet scrubber is expected to be low (both ESP and FF have very high particle removal efficiencies). Also by using a semi-dry scrubbing system adsorption in the fabric filter is greatly improved and can affect the concentrations of class III heavy metals, such as mercury. On the other hand, it can be easily justified to use this power plant for heavy metal reduction measurements. According to (Maunula, et al., 2016; Valmet, 2016) waste fuel has typically the highest concentrations of heavy metals in comparison to other generic fuels, thus providing larger concentrations which are more easily detected. Fuel type has been the main incentive to investigate heavy metal reduction in this power plant. Furthermore, investigating heavy metal reduction under actual industrial condi-

tions eliminates issues in phenomena scale-up, although measurement inaccuracies become more prominent.

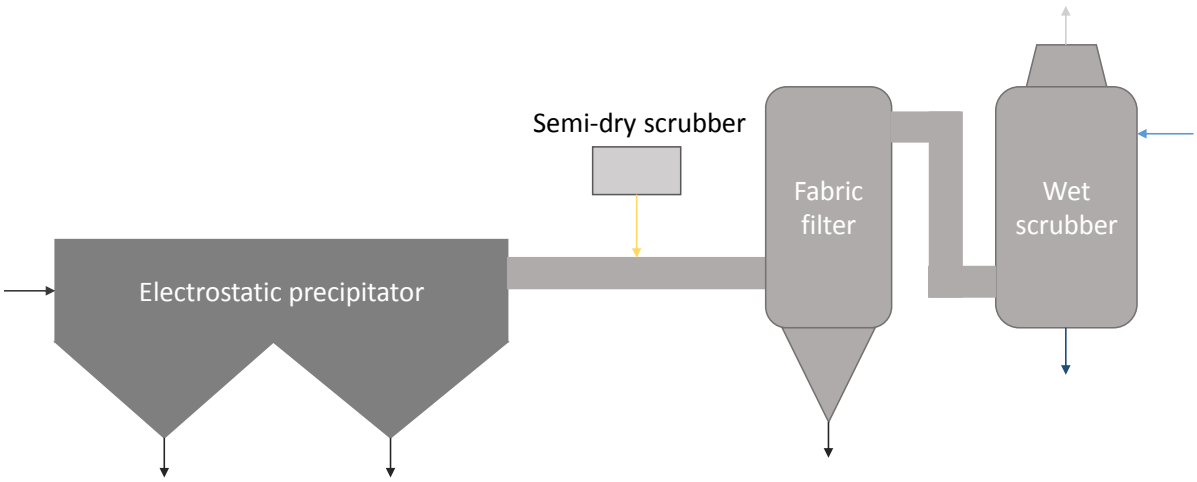

Figure 22: *Layout of environmental systems in power plant T* (Valmet, 2016)

The flue gas cleaning system of the power plant is described in Figure 22. Figure describes the order of flue gas control systems and their inflow and outflow streams. Electrostatic precipitator and fabric filter outflow streams consist only of solid particles, semi-dry scrubber feeds the scrubbing sorbent into the flue gas duct. Wet scrubber inflow and outflow streams have been presented in the previous subchapter. Due to sensitivity between semi-dry and wet scrubber, it was impossible to change scrubbing liquid pH between cases. This lead to combining these cases into a one long measurement case.

5.2.2 Power plant K

Power plant K is a large CHP power plant using biofuel and peat mixture as fuel. Biofuel used is wood based and can vary from forest residue, stem chips, and whole wood chips to bark and recycled wood. Power plant boiler is a bubbling fluidized bed boiler. Since the fuel used is a mixture, it can have varying characteristics, similar but in a much smaller scale when compared to power plant T waste fuel. The flue gas control system in this power plant is simple and straightforward. It consists of SNCR system, where urea is sprayed into the flue gas duct in order to reduce nitrogen oxides into nitrogen gas. Electrostatic precipitator is used to remove particle matter. The final part of the environmental control system is a two-stage wet scrubber. It consists of a spray tower and a packed-bed scrubber, similar to the wet scrubber in power plant T. Power plant K information has been compiled into Table 19 and flue gas control system layout in presented in Figure 23. (Maunula, et al., 2016; Valmet, 2016)

Table 19: *Power plant K basic and environmental system information* (Valmet, 2016)

Boiler	Power [MW]	Pre-control	Wet scrubber	Fuel	LHV [MJ kg^{-1}]	Cases
BFB	245	SNCR, ESP	Two-stage: Spray tower, packed-bed	biofuel, peat	10	K1, K2, K3, K4

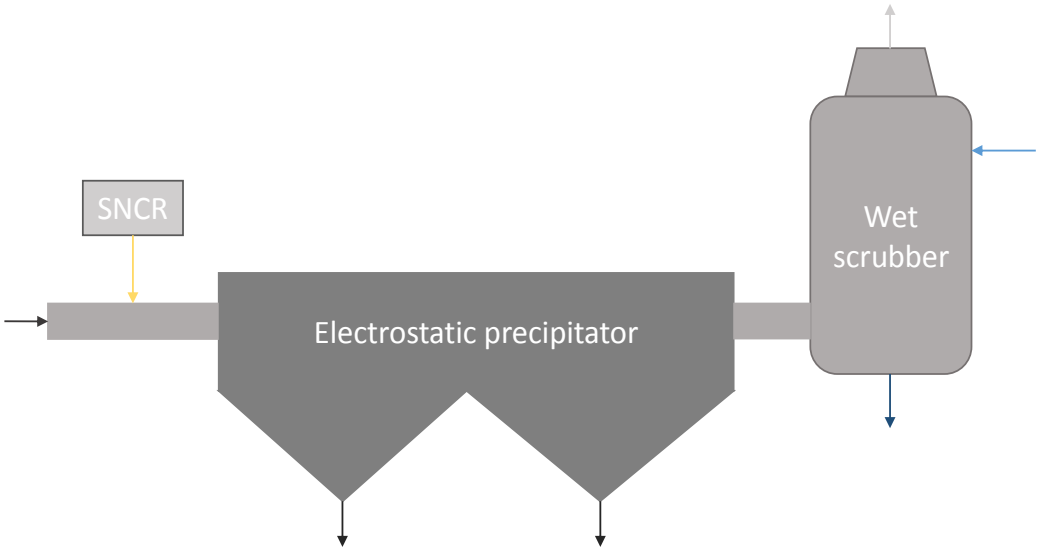

Figure 23: *Layout of environmental systems in power plant K* (Valmet, 2016)

Power plant K has both advantages and disadvantages in relation to heavy metal reduction measurements. Advantages include less-intensive flue gas control before the wet scrubber and controllable particle reduction. The main disadvantage is the lack of a significantly heavy metal laden fuel. Wood based biofuel and peat are not particularly significant in regards to heavy metal emissions, but heavy metal reduction measurements are expected to be possible based on results received in previous measurement data survey (subchapter 4.2). The measurements in power plant K do not greatly differ from the general measurement plan, since it is merely an expanded version of it. Instead, the measurements described in subchapter 5.1.1 are performed twice. First measurements are performed under normal power plant operating parameters (2 cases), then particle reduction efficiency of electrostatic precipitator is lowered by reducing current and shutting off ESP fields and then measurements are repeated (two cases). In these two later cases pH is not changed and only further electric current changes are made. By investigating heavy metal reduction under a greater particle matter load, reduction cut-off limits can be determined and due to larger heavy metal concentrations and measurement accuracy is expected to be significantly improved.

6. RESULTS AND DISCUSSION

This chapter consists of discussion on all aspects of the thesis ranging from calculation tools to data survey and measurement campaign. Calculation tool discussion focuses on two distinct aspects: functionality and potential. In each subchapter a specific calculation approach is discussed by investigating partial successes, failures, and the reasons behind them. Also, the potential aspect is evaluated in reference for future expansion. Data survey discussion evaluates the impact of general issues in the survey and methods to improve future data surveys. Finally, the measurement campaign discussion consists of two separate sections: measurement campaign data analysis and general discussion. The measurement data is analyzed and compared in the first section and an overall discussion and future improvements can be found in the latter portion.

6.1 Discussion of calculation tools

6.1.1 Thermodynamic equilibrium and kinetic tool

The creation and use of the modeling tool faced a plethora of uncertainties, challenges, and problems but it was also to confirm some speciation and reduction phenomena described in publications. As an overview the approach to modeling failed to produce a cohesive and accurate modeling tool, but some sub-models did produce fair results.

The basis of the tool was to examine thermodynamic equilibrium and supplement findings with kinetics calculations where available. This equilibrium assumption is rarely a valid approximation and even if the modeling tool would have been complete success otherwise, its results may still have been lacking in confidence. A better approach would have been to investigate more accurately a section of this case, for example the speciation of mercury in flue gas as was conducted in (Edwards, et al., 2001) or a thermodynamic study of stable forms for different mercury compounds as was investigated in (Aunela-Tapola, et al., 1998).

Discussion of specific issues and challenges faced is divided into three parts: data availability and compiling, functionality of calculations, and finally usefulness of produced results. Data availability was fairly good for temperature dependent log K values and was the starting point of this modeling tool. Using (Barin, 1989) data was simple since it was extensive and comparable, but problems in finding proper values for aqueous solutions and liquid water proved difficult. In the brief study of kinetic modeling, data seemed more available but it suffered limitations because every publication had only

certain reaction pathways and data for them. Thus creating a tailored kinetic model that is complex enough proved too time-consuming. Also creating correlations based on the data available provided varying results. The temperature range was greatly reduced by limitations caused by some component data. Although correlations were set to match the measurement data well, their accuracy is still in question in very low and high temperatures.

Calculations proved simple and robust to set up and run, but in practice the thermodynamic and kinetic tool proved unusable due to the very large or small values calculated for the equilibrium constant. Only reactions in equations 7 and 16 managed to provide usable information. At 500 K their K_p values were 0.09 and $2.98*10^{19}$, respectively. With this information can be confirmed the fact that mercury oxide does not oxidize easily at lower temperatures and mercury chloride is a stable form of oxidized mercury at lower temperatures that matches the findings in (Aunela-Tapola, et al., 1998).

Reactions 17 – 19 also suffered from very large equilibrium constant values in the range of 10^{-300}, 10^{20}, and 10^{120}, respectively. Reactions influencing the aqueous solution speciation (equation 21-24) also suffered from the same problem. Their K constants ranged from 10^{-2} to 10^{-4} and 10^{4} to 10^{40}. Very small or large constants led to three different problems in tool functionality. The first issue deals with the set limits in equilibrium concentrations. Since reagent concentrations are limited to zero and the inlet concentration, iterations had a very narrow window to work with and thus typically reactions happened completely or not at all. Second problem was caused by the iteration problems. In some cases, iterations failed to find any change in functions when changing equilibrium concentrations and this led to them producing random values and breaking the overall fluidity of the tool. Reason for this problem may have been the lack of certain important reactions and the use of overall reactions. Also the phase of some components is in question; phase transformation was not investigated here and may be a key aspect in more comprehensive modeling.

Despite of these problems thermodynamic modeling can be useful in determining reaction pathways and stable materials in future modeling. Solubility calculations were not integrated into the calculation due to the poor functionality of 7, 16 - 19 equations, but they produced data that was expected: elemental mercury proved to be insoluble and mercury(II) chloride very soluble. It was also possible to provide correlation between temperature and solubility, although it can also be found just by observing at data from (Clever, et al., 1985).

The kinetic behavior investigation proved to be insufficient from the very start when compared to actual kinetic modeling. In (Edwards, et al., 2001) kinetic modeling was conducted with 60 reactions and 21 species. Building the model was scrapped early due to a great number of problems involved: need for a large data sample, Arrhenius equation parameters, and additional thermodynamic equilibrium investigation for reactions

included. And also, due to the large exponents present in kinetic parameters for Arrhenius equation, more powerful calculation software would probably be required. The kinetic modeling itself failed to provide any results at all, but investigation of data gathered from (Edwards, et al., 2001) proved that there are many fast pathways for $HgCl_2$ formation, which supports the large presence of mercury chloride in cooled flue gas (Aunela-Tapola, et al., 1998).

In summation, the modeling tool failed to produce results in its complete form but many lessons were learned in regards to sensitivity analysis, confirming certain aspects of mercury reduction and speciation, and challenges in optimization of modeling scale and accuracy. For example, the greatest issue was finding suitable data and enough reaction pathways to create a meaningful modeling case, but still keeping the width of the analysis in control. Another issue proved to be the sensitivity of the created tool. In this case no sensitivity analysis was conducted due to most reactions happening despite a change in temperature to their full extent or not at all. Some aspects of the tool proved fairly useful. For example, thermodynamic investigation of reaction pathways i.e. determining whether or not a reaction is possible. In addition, solubility of gases and ionic compounds seemed to work well. By developing an improved kinetic and thermodynamic tool, it could be further expanded by using the reaction calculations in CFD modeling, multi-pollution control (NO_x & SO_2) investigations, and scrubbing liquid oxidant research.

6.1.2 Existing modeling tools

Both commercial modeling programs tested have potential and limitations in their usage in regards to the heavy metal reduction calculation. When the speciation, reduction, and chemical behavior is scrubbing liquid is simplified to a certain level, these programs can be effective modeling tools. By completely skipping speciation of heavy metals and simply having a set amount of class I and II heavy metals in particle form and selected class III heavy metals and their compounds handled through solubility, these tools could provide reasonable results. Class I and II heavy metal reduction would completely depend on particle removal. Chemical behavior of heavy metals would have to be handled through an additional calculation block, for example with equilibrium or kinetic reactor block. These calculations would be required to set up with additional data and user defined functions and reactions, but it could be integrated into this program in order to have a more consistent and comprehensive modeling system. A similar reactor set up could be created to model the speciation of heavy metals in flue gas, but a better option would be to modify existing CFD calculation tools by adding kinetic subsystems to predict speciation and export the data into Chemcad or Aspen plus. Both of these programs have also a powerful sensitivity analysis tool, which could easily produce a great deal of valuable information, since there is a remarkable amount of variables to test. In their

current form they are merely suited to examine the particle removal from flue gas. In this regard Aspen plus has more parameters influencing the reduction procedure.

These programs also contain a great deal of unsolved issues and deficiencies that can greatly hinder the creation of a comprehensive modeling tool. The very first great issue is the lack of many important scrubber types and parameters. Chemcad only had venturi scrubber and Aspen plus had venturi scrubber and spray tower. The lack of calculation blocks for scrubbers greatly limits the usefulness of a modeling tool. In subchapter 2.3.2 some typical scrubber designs were presented and either of these programs did not even have all of these. Although both did have a packed-bed calculation block, it was not set up for particle removal and it separates all the particle matter into the liquid stream. Packed-bed modeling seemed very comprehensive but since it was not able to handle solid particles it was not useful. In addition, problems in detailed spray tower modeling cause problems. There is no option to choose the configuration whether it is cocurrent, cross-current, or countercurrent. Although the lack of these blocks and details are not dead ends, they do raise the bar quite high before choosing which program to use as a platform for the modeling tool.

Another massive problem hindering the creation of a more comprehensive tool is the lack of many heavy metals and their components. This mainly affects the speciation and chemical behavior of heavy metals and it can be avoided by simplifying modeling greatly. This simplification in essence means that heavy metal reduction is solely estimated through particle removal. The problems in this are numerous and significant because mercury is one of the most important heavy metal pollutions and most of it cannot be accounted in this modeling approach, also chemical behavior of heavy metals cannot be estimated. Since class III heavy metal reduction has to be examined through solubility, heavy metal speciation becomes extremely important in order to determine reduction efficiencies. The lack of heavy metal compounds affects directly the speciation, solubility, and chemical reactions taking place in the scrubbing liquid. Heavy metal reduction is also affected by chemical reactions involving heavy metals that occur in the scrubbing liquid. These reactions can affect the re-emission rates of class III heavy metals, complexation, and precipitation of heavy metal compounds in wastewater. In order to be able to examine these phenomena, calculation blocks need to be able to handle reactions between two sub-streams and take into account complex chemistry involving numerous reactions.

In summation the current level of modeling fidelity that can be achieved with these two programs is fairly good for particle removal, but conflicted for gas solubility, particularly for Aspen plus. Chemcad produced mixed results in regards to solubility. The lack of some class III heavy metal components in Chemcad and the poor functionality in Aspen plus has a significant negative impact on the feasibility of heavy metal reduction. Also the small quantity of different scrubbers and configurations limits greatly the usefulness of both programs, even if all other issues are solved. A larger pool of functional scrub-

ber types that take into account particle removal and gas solubility would be a good start. In addition, inclusion of all relevant heavy metals and their common and stable species would help with solubility, precipitation, and complexation modeling. As discussed before, speciation should be calculated with CFD (computational fluid dynamics) programs and its results transferred into one of these programs. This would also be greatly helped by the addition of more heavy metal species. If no actions are taken to improve these programs, they could still be used to model some reduction behavior. Both Chemcad and Aspen Plus can calculate class I and II heavy metal reduction fairly well through particle reduction in venturi scrubber, Aspen plus can also do the same for a spray tower. Class III heavy metal reduction is not possible with Aspen plus and only elemental mercury solubility can be poorly examined with Chemcad.

6.1.3 Lumped model –tool

Lumped modeling tool has potential in its agile format and ability to handle the overall reduction process in a simplified manner. Other tools investigated could not reach these significant achievements. On the other hand, this tool has some shortcomings when compared to the initial expectations. For example, this model has limited input parameters and interactions between them and accuracy of produced results is dependent on measurement data, which are characteristic issues with lumped modeling.

The lumped model calculation tool is a simple and easily modifiable tool, that can be used to estimate the reduction process in a general sense, but also it can be specified to focus on a certain type of scrubber, fuel, or boiler. This can be achieved by creating groups of reduction coefficients for different types of conditions. Through further development, this tool can be used without user modification to have previously stated focuses as input values. Also by creating correlations between reduction coefficients and input values such as temperature, or by adding new input parameters correlating with coefficients, this tool could be used to model the sensitivity of the system, although requiring a very large amount of measurement data. By having a larger and detailed supply of measurement data, reduction coefficients could be split into various parallel and series connected sub-coefficients that can predict the reduction achieved through different phenomena, such as solubility, large particle reduction, submicron particle reduction, and finally the re-emission of class 3 heavy metals. A great improvement would also be to improve and refine the effect of residence time on reduction efficiency by creating an overall correlation of power plant load on reduced residence time.

This tool uses remarkable simplifications in its calculation, which is typical in lumped modeling. Significant issues with fidelity can rise when using reduction coefficients based on general reduction efficiencies or specific reduction measured in few scrubbers. Either data source can lead to significant errors in calculation results due to some phenomena greatly affecting reduction efficiency in the investigated scrubber that is not present in values used as coefficients, or vice versa. A rigorous testing campaign will be

required to determine the fidelity of results for different reduction coefficient groups in order to define limitations for this tool.

In summation, upsides of this tool are its ability to calculate overall reduction of heavy metals and its agile platform that can be easily modified and improved with additional data. The major downside of this calculation tool is its foundation in lumped modeling, due to the large generalizations involved in using reduction coefficients. These simplifications remain at the core of this model, even after addition of sub-coefficients to model different behavior. In order to improve the confidence of the modeling tool, reduction coefficient determination requires a large amount of measurement data to produce detailed and system specific reduction modeling. The data survey and measurement campaign partly act as a preliminary investigation into determining detailed reduction coefficients.

6.2 Discussion of data survey

6.2.1 Data from publications

As an overall survey to find reduction efficiencies from public data some findings were made and the useful type of data was quickly identified. The measurements discussed in the subchapter 4.1 show that trying to find accurate and applicable reduction coefficients through measurement data publications can be difficult and problems varying from case specific behavior to simple inaccuracies in concentration measurements can become insurmountable. The most significant issue in measuring heavy metals in wet scrubbers is the already small concentrations in inflow flue gas, due to flue gas precontrol and low heavy metal concentrations in fuels. Reduction efficiencies presented in various Tian publications discuss heavy metal reduction in wet scrubbers and wet flue gas desulfurization units separately and no distinction is provided between these two devices. A more comprehensive support data package is also necessary to determine the comparability between cases, but such information was unavailable. Comparisons between cases can be made but the fidelity of the results is in question. Another very large problem arises from general vague description of processes, devices, and operating parameters. Information about devices such as boiler and scrubber type was rarely available, and similar problem was found while searching for operating parameters. While there was some information available, data to calculate heavy metal mass balances was systematically unavailable.

Although data survey in general was not a great success due to the lack of large samples of data, poor descriptions, and support data availability some preliminary reduction coefficients can be acquired based on this data. By comparing reduction efficiencies from Tables 12 and 13 to particle matter reduction achieved during measurements in Cordoba

1 and 2 some general reduction coefficients can be created, albeit their function in lumped model –tool is at best a very rough estimation of heavy metal behavior.

In summation data survey was conducted on publicly available data, focusing on publications. It resulted in scarce and various findings mainly focused on heavy metal concentrations in fuel and water flows. Sufficient measurements conducted to measure heavy metal concentrations in flue gas were very scarce, although some data presenting calculated reduction efficiencies, scrubber reduction is typically lumped with other air control systems, such as ESP or fabric filters. This was expected since wet scrubbers are primarily used at the tail-end of the flue gas control procedure and they are rarely used alone. Other problems included severe lack of supporting and operating data for power plants in order to calculate mass balances for scrubbers and differentiate measurement cases and typical reduction rates into different groups, for example based on scrubber or boiler type. Through novel manipulation of data acquired some preliminary and generic reduction rates were produced based on limestone scrubbers in coal-fired power plants.

6.2.2 Previous measurement data

Overall issues found during this data survey were similar in comparison to public data survey. As before, main issues included data availability, measurement confidence, and comparability. In the scope of this survey comparability was improved due to the fact that support data was readily available and had more comprehensive parameters. Also data availability was better, which can be seen in previous measurement data survey having almost twice as many cases as public data survey had. In this survey, some issues arose in these three fields as well. Even this data survey suffered from a lack of measurement cases and variety in power plant parameters, such as boiler type. A larger amount of comprehensive measurement cases would have helped greatly in determining differences between plant parameters, measurement inaccuracies, and heavy metal speciation. There was also a lack of support data in every case investigated and no mass balances were calculated to provide reduction efficiencies and estimating their fidelity. Another missing support data values include heavy metal concentrations in fuel, particle reduction rates, and condensate outflow rates. Measurement case data and reports were fragmented and scattered in many cases and had were pieced together from many databases and reports, which adds to issues in measurement confidence. For example, supporting data was gathered from various sources and many cases for the same plant were acquired from measurements conducted years or even decades apart.

For future reference and a baseline for measurement campaign, some guidelines are drawn to determine a proper heavy metal reduction measurement case in a wet scrubber. Firstly, data needed to calculate heavy metal mass balance in the scrubber is vital. Heavy metal measurements need to be taken from the flue gas entering and exiting the scrubber, also heavy metal water samples from condensate outflow points are taken, depending on whether the scrubber has multiple sections. Supporting data is also re-

quired to calculate the mass balance of the scrubber. This requires gas inflow and outflow volume flowrates, condensate outflow volume flowrate, and gas parameters, such as thermodynamic data and gas composition (T, p, O_2-mole fraction, moisture fraction). In addition, a detailed power plant parameters and fuel data can greatly increase the comparability of results between different power plants. In order to improve the effectiveness of the data surveys themselves, a great help would be a data gathering plan that would set boundaries for the type and locations of data gathered. Data compiling should be conducted after all data has been gathered due to having multiple revisions performed to the data template during compiling the data.

In summation, previous measurement data survey produced an acceptable amount of measurements in fairly well defined and varied power plants. The preliminary idea was to calculate heavy metal mass balances for scrubber flue gas and condensate flows to determine reduction efficiency and credibility of results. Although this was not achieved due to deficiencies in measurement and support data, reduction values were calculated, evaluated, and their fidelity analyzed. In comparison to public data survey, this survey used a greater amount of data points, significantly better support and measurement data, and it also produced more credible reduction coefficients. Analysis contains a detailed investigation of heavy metal classification behavior, estimation of measurement data accuracy and comparability between different power plants. In addition, the formation of the reduction coefficients and methods used in data filtration is presented and discussed.

6.3 Measurement campaign data analysis

6.3.1 Power plant T

Next two subchapters contain a presentation and analysis of plant specific results in power plants T and K. These subchapters' core idea is to evaluate the heavy metal mass balances calculated with flue gas and condensate concentrations and volume flowrates. Mass balances are then used to investigate reduction rates, gas proportions, and measurement errors. Significant information regarding power plant operations and measurement process is also presented here.

Power plant T had very steady operating parameters, particularly condensate parameters had very little fluctuation. As described in the subchapter 5.2.1, wet scrubber condensate flow was circulated back to the semi-dry scrubber, which prevented any meaningful process changes to warrant two measurement cases. This lead to combining the planned cases into a one long measurement. Due to inconsistent fuel properties, the grate furnace flame pattern did change during the measurement case, which had some effect on the flue gas temperature at the wet scrubber inlet. Flue gas measurement instrumentation faced some difficulties during this measurement case. Measurement location before the

wet scrubber was poor, due to its location in a duct bend. The location also made in impossible to insulate and heat the measurement probe, which lead to condensation in the probe condensation bulb. These issues can affect measurement results but any clear effects are difficult to identify.

Measurement case T mass balance data is presented in Table 20. Gas proportion column lists components' heavy metal gas phase concentration in proportion to total concentration. It has to be stated that gas phase is likely to contain a significant amount of smaller particles. Inflow and outflow mass flowrates are heavy metal mass flowrates in flue gas. Condensate mass flowrate is heavy metal mass flowrate in condensate exiting the scrubber. Reduction efficiency column contains reduction rates calculated by using flue gas heavy metal mass flowrates. Mass balance evaluation 1 contains balance evaluation using subtraction and evaluation 2 uses division. Evaluation 1 is expected to approach zero and evaluation 2 to approach one.

Table 20: *Power plant measurement case T*

Element	Gas proportion [%]	Inflow mass flowrate [µg s^{-1}]	Outflow mass flowrate [µg s^{-1}]	Condensate mass flowrate [µg s^{-1}]	Reduction efficiency	Mass balance eval. 1 [µg s^{-1}]	Mass balance eval. 2
As	46.154	24.388	12.300	0.509	0.496	11.579	0.525
Br	18.561	1155.080	126.000	0.000	0.891	1029.080	0.109
Cd	92.857	3.484	2.700	0.102	0.225	0.682	0.804
Co	48.182	294.800	5.700	0.102	0.981	288.998	0.020
Cr	78.049	21.976	18.900	0.713	0.140	2.363	0.892
Cu	73.333	361.800	90.000	0.509	0.751	271.291	0.250
Hg	88.889	2.412	1.500	0.051	0.378	0.861	0.643
Mo	78.740	67.000	114.000	0.917	-0.701	-47.917	1.715
Ni	86.466	72.360	12.900	0.917	0.822	58.543	0.191
Pb	85.149	134.000	36.000	0.509	0.731	97.491	0.272
Sb	95.238	22.512	19.500	0.509	0.134	2.503	0.889
Tl	50.000	0.268	0.900	0.102	-2.358	-0.734	3.738
V	75.000	1.876	3.300	1.019	-0.759	-2.443	2.302
Zn	91.837	787.920	183.000	5.298	0.768	599.622	0.239

Using mass balance evaluation methods, it can be seen that mass balances are considerably poor and indicate issues particularly in measurement accuracy. Mass balance evaluation 1 shows in all cases remarkable deviations from the expected value of zero and in most cases these deviations are larger than heavy metal flow rate in condensate. In addition to measurement inaccuracies, this indicates significant issues in the combination of different measurement standards. Mass balance evaluation 2 shows more clearly the

same problem. None of these mass balance values comes close to the expected values of one, which is caused by similar issues as in mass balance evaluation 1. In comparison to mass balances calculated in (Cordoba, et al., 2012), very significant fluctuations can be found in case T1. In (Cordoba, et al., 2012) all mass balances (evaluation 2 method) are between 0.66 and 1.34, which is a very tight grouping in comparison. Also, median for mass balances in the publication is 1.00 – 1.01. In this measurement campaign, a difference of 30 to 40% would have been acceptable, but every compound except chromium, cadmium, and antinomy has larger values. These three heavy metals have very small reduction rates, which seems to improve mass balance accuracy. Lower reduction rates in all cases seem to correlate with better mass balance evaluation 2 values. This represents a great problem in the core idea of the mass balance calculations. As heavy metal reduction rates increase, a larger heavy metal flowrate in condensate is expected, but such correlation is not present in these measurements. This can be explained through very small concentrations in both flue gas and condensate. When concentrations are small, it becomes more difficult to detect small deviations near detection limits. When dealing with very small concentrations, measurement accuracies and different sampling methods are greatly affected by systematic errors. Poor measurement accuracy is also supported by measurement system data, since the probe before the scrubber suffered from multiple problems, which leads to uncertain inflow concentrations. Measurements taken after the scrubber only suffered from detection limit values, which was unavoidable in this power plant.

Due to rigorous particle control before the wet scrubber, direct speciation investigation is not feasible. This is caused by high gas proportions for class I & II heavy metals. There seems to be no correlation between gas proportion and reduction efficiency in specific heavy metal classes. Cobalt is the only class I heavy metal and has a surprisingly high gas proportion, but its reduction rate seems unaffected.

For class II heavy metals gas proportions and reduction rates range from 49% to 91% and 0.14 to 0.82, respectively. No definitive conclusions can be determined from such investigations, but it can be stated that condensation behavior is also dependent on heavy metal species and not only on heavy metal class. Reduction rates seem to be incomparable between heavy metal species, since no similar behavior in regards to gas proportion emerge. For example, chromium has a gas proportion of 78% and reduction rate of 0.14 and copper has 78% and 0.75, respectively. In some cases, similar behavior can be identified. For example, nickel and lead have similar gas proportions, inflow, and reduction rates. To a lesser extent, zinc and copper have also similar reduction values, but their inflow rates are much higher and gas proportions deviate considerably. Higher gas proportion does not seem to correlate inversely with reduction efficiency, which will be investigated further in chapter 6.3.3. Particle reduction rate was 0.88 during this case, but only few class I or II heavy metals could reach similar reduction rates. These heavy metal species include cobalt and nickel, and also to a lesser extent zinc and lead.

Similar reduction for class I heavy metal when compared to particle reduction is expected and for class II heavy metals differences in reduction suggest certain condensation behavior. For situations where heavy metal reduction is lower, condensation on smaller particles is more prevalent.

Mercury and bromine had very different gas proportions, which was very unexpected. According to theoretical understanding, they both have class III behavior, but bromine had very low gas proportion. In addition, bromine had quite high concentrations, which rules out measurement inaccuracies. There are two possibilities for such unexpected behavior, bromine may react with specific compounds in the combustion process that can condensate before the scrubber or fly ash has selective adsorption characteristics specifically for bromine. Mercury class behavior and reduction rate was expected. Active carbon particles will adsorb some elemental mercury in the semi-dry scrubber, which increases the proportion of oxidized mercury flowing in to the wet scrubber. This leads to a more defined expectation for mercury reduction, which in this case could have been even higher, but still acceptable.

6.3.2 Power plant K

Power plant K operating parameters fluctuated somewhat during all measurement cases, due to constant changes in electricity and heat consumption, but anything alarming was not detected. During all cases boiler thermal power was between 25 – 30% of maximum and the fuel used was a blend of biofuel (70%) and peat (30%). During measurement case K1 and first half of K2 electricity production was maximized by minimizing condensate flow from the wet scrubber's condensing stage (stage 2). This lead to low condensate flows in general, but both stage one and two condensate flows had a few large spikes. Between cases K1 and K2 scrubbing liquid pH was adjusted from 5.5 to 7 by increasing sodium hydroxide flowrate. Scrubbing liquid was kept at 7 pH throughout the rest of the measurement cases. Between cases K2 and K3 two parallel fields in the electrostatic precipitator were switched off leaving only two fields charged. This increased particle matter concentration fivefold, but was roughly 20 times lower than expected. This was caused by minimal boiler thermal power. This issue led to case K3 measurement time being too short. To further increase particle matter concentration in flue gas, electric current to the two charged ESP fields was halved. This increased particle matter concentration 15 times when compared to K1 and K2 concentrations. Unlike case K3, measurement case K4 had normal measurement time, similar to K1 and K2 cases. In power plant K measurement locations were excellent, probe angles in regards to flue gas flow were good, and probes functioned in standard assembly. Flue gas temperature at wet scrubber inlet remained stable during measurement cases, but a small drop was noticed between cases K2 and K3. Mass balance data for cases K1 – K4 is presented in Tables 21 – 24.

Table 21: *Power plant measurement case K1*

Element	Gas proportion [%]	Inflow mass flowrate [µg s^{-1}]	Outflow mass flowrate [µg s^{-1}]	Condensate mass flowrate [µg s^{-1}]	Reduction efficiency	Mass balance evaluation 1 [µg s^{-1}]	Mass balance evaluation 2
As	4.545	11.836	1.425	17.026	0.880	-6.615	1.559
Br	96.154	6456.000	893.000	0.000	0.862	5563.000	0.138
Cd	33.333	3.228	2.850	2.365	0.117	-1.987	1.616
Co	93.443	32.818	15.200	10.164	0.537	7.454	0.773
Cr	70.000	21.520	9.500	53.420	0.559	-41.400	2.924
Cu	73.333	242.100	80.750	27.424	0.666	133.926	0.447
Hg	99.698	177.540	85.500	1.377	0.518	90.663	0.489
Mo	73.034	96.840	47.500	32.623	0.510	16.717	0.827
Ni	85.714	30.128	20.900	360.684	0.306	-351.456	12.665
Pb	49.123	59.180	15.200	22.225	0.743	21.755	0.632
Sb	96.512	46.268	61.750	6.627	-0.335	-22.109	1.478
Tl	50.000	1.076	0.950	1.325	0.117	-1.199	2.115
V	18.182	5.918	2.850	13.254	0.518	-10.186	2.721
Zn	56.061	710.160	194.750	1318.356	0.726	-802.946	2.131

Table 22: *Power plant measurement case K2*

Element	Gas proportion [%]	Inflow mass flowrate [µg s^{-1}]	Outflow mass flowrate [µg s^{-1}]	Condensate mass flowrate [µg s^{-1}]	Reduction efficiency	Mass balance eval. 1 [µg s^{-1}]	Mass balance eval. 2
As	12.500	3.073	1.077	23.726	0.650	-21.730	8.071
Br	96.511	5926.500	728.770	0.000	0.877	5197.730	0.123
Cd	50.000	1.317	2.872	1.812	-1.181	-3.367	3.557
Co	94.915	25.901	12.206	19.409	0.529	-5.714	1.221
Cr	84.848	13.170	19.027	302.347	-0.445	-308.204	24.402
Cu	41.860	188.770	17.232	47.452	0.909	124.086	0.343
Hg	99.415	74.630	89.750	0.906	-0.203	-16.026	1.215
Mo	79.487	52.680	39.490	120.773	0.250	-107.583	3.042
Ni	85.714	15.365	20.463	45.308	-0.332	-50.406	4.281
Pb	68.605	37.754	12.206	23.726	0.677	1.822	0.952
Sb	98.750	35.120	46.670	9.062	-0.329	-20.612	1.587
Tl	50.000	0.878	1.077	1.812	-0.227	-2.011	3.291
V	50.000	1.756	2.154	18.123	-0.227	-18.521	11.547
Zn	68.269	456.560	140.010	726.782	0.693	-410.232	1.899

Table 23: *Power plant measurement case K3*

Element	Gas proportion [%]	Inflow mass flowrate [µg s^{-1}]	Outflow mass flowrate [µg s^{-1}]	Condensate mass flowrate [µg s^{-1}]	Reduction efficiency	Mass balance eval. 1 [µg s^{-1}]	Mass balance eval. 2
As	3.297	27.118	5.168	16.772	0.809	5.178	0.809
Br	90.009	6317.600	1054.880	0.000	0.833	5262.720	0.167
Cd	25.532	14.006	3.952	1.280	0.718	8.774	0.374
Co	31.818	131.120	13.680	6.984	0.896	110.456	0.158
Cr	59.633	65.560	139.840	94.555	-1.133	-168.835	3.575
Cu	87.597	384.420	136.800	33.544	0.644	214.076	0.443
Hg	94.017	104.300	106.400	11.100	-0.020	-13.200	1.127
Mo	44.578	247.340	45.600	59.472	0.816	142.268	0.425
Ni	95.445	140.060	28.880	364.203	0.794	-253.023	2.807
Pb	27.273	232.440	88.160	11.587	0.621	132.693	0.429
Sb	94.156	92.380	60.800	6.401	0.342	25.179	0.727
Tl	42.857	2.086	3.344	1.280	-0.603	-2.538	2.217
V	31.373	15.198	1.824	12.802	0.880	0.572	0.962
Zn	65.647	2142.620	957.600	371.417	0.553	813.603	0.620

Table 24: *Power plant measurement case K4*

Element	Gas proportion [%]	Inflow mass flowrate [µg s^{-1}]	Outflow mass flowrate [µg s^{-1}]	Condensate mass flowrate [µg s^{-1}]	Reduction efficiency	Mass balance eval. 1 [µg s^{-1}]	Mass balance eval. 2
As	0.901	40.040	37.840	33.023	0.055	-30.823	1.770
Br	96.688	8117.200	822.160	0.000	0.899	7295.040	0.101
Cd	3.704	19.656	16.856	4.013	0.142	-1.213	1.062
Co	44.086	33.852	9.288	6.086	0.726	18.478	0.454
Cr	32.540	47.320	299.280	87.964	-5.325	-339.924	8.184
Cu	56.604	192.920	79.120	43.389	0.590	70.411	0.635
Hg	97.561	58.240	68.800	19.754	-0.181	-30.314	1.521
Mo	38.326	80.080	34.400	66.046	0.570	-20.366	1.254
Ni	81.356	43.680	26.144	229.975	0.401	-212.439	5.864
Pb	4.382	371.280	79.120	38.206	0.787	253.954	0.316
Sb	79.137	50.960	44.720	7.108	0.122	-0.868	1.017
Tl	12.500	3.276	2.408	1.422	0.265	-0.554	1.169
V	4.110	26.572	9.288	24.583	0.650	-7.299	1.275
Zn	89.503	2635.360	550.400	698.812	0.791	1386.148	0.474

Mass balance evaluations proved inaccurate in all measurement cases in both evaluation 1 and 2. Method 1 shows mass balance differences larger than one of the heavy metal mass flow rates in most cases, typically condensate heavy metal flow rate. In order to validate measurements with mass balance methods evaluation 1 should calculate values at least ten times smaller in comparison to the smallest heavy metal flow rate. Also, mass balance evaluation 2 should produce values very close to one. Method 2 shows that for most heavy metal species in all cases are either significantly larger or smaller than the expected value. Similar issues can be found between (Cordoba, et al., 2012) and cases K1 – K4 as were found between the publication and T1. Heavy metal mass balances deviate a great deal in K cases in comparison to (Cordoba, et al., 2012). These differences from expected values seem to somewhat correlate inversely with low reduction rates, but low reduction rates do not guarantee small deviations in mass balances and in some cases high reduction rates can result in accurate mass balances. This can be explained by the differences in measurement method from flue gas and condensate, which was presented in the previous subchapter (6.3.1). When comparing mass balance evaluation 2 values between cases, it seems that in higher particle matter flow rate mass balance values are closer to accurate values. The amount of these values rises from 1 to 5 between cases, but both cases 2 and 3 have 2 accurate mass balances. The change in particle matter between cases 2 and 3 does not seem to be very significant in this regard. Since there is no great improvement in mass balance accuracy between cases, even in increased particle matter conditions, it can be stated that heavy metal content in fuel is too low to acquire data for further calculations. In addition to systematic errors in combining different measurement methods (flue gas and condensate measurements) and small concentrations in flue gas to begin with, the plant operations were continuously changing during and in between measurement cases in order to match heat and power consumption. This is thought to be a significant cause for measurement inaccuracies as well. Process parameters may change before or after condensate sampling, which will lead to highly varied results in accuracy of the mass balances. This behavior was quickly identified and will be taken in to consideration in further research.

Particle reduction before the wet scrubber was controlled in these cases, which should have led to a significant decrease in gas proportion for class I & II heavy metals, but in the case for copper, nickel, antimony, and zinc no significant decrease takes place and instead in some cases an increase happens. Investigating cobalt (class I heavy metal) reduction can be easily identified. As particle matter increases in cases 3 and 4, gas proportion is lower and reduction rate is increased. This behavior was expected and matches theoretical understanding well. Further investigation into class II heavy metal behavior shows that arsenic has very low gas proportions, but due to arsenic contamination during measurement sample analysis, cases K1 and K2 have to be disqualified, thus no speciation analysis can be conducted on arsenic. Cadmium, lead, thallium, and vanadium reach very small (<15%) gas proportion in case K4, which indicates that they are condensing on medium to large particles, that are captured by the filter in the measuring

probe. Reduction rates for these heavy metals only form unclear patterns. Cadmium and thallium produce highly varied, but typically very low or even negative reduction rates. Lead and vanadium have medium-high reduction rates in most cases (0.6 – 0.8), but they do not correlate with their respective gas proportions. To a lesser extent chromium, copper, and molybdenum have a midrange (30 – 60%) gas proportion in case K4, which indicates a preference on smaller particles. Chromium produces highly inconsistent and often negative reduction values and cannot be further investigated. Copper had relatively steady reduction rates, but no consistent correlation with gas proportion. Molybdenum had both inconsistent reduction rates and correlation with gas proportion. For antimony and nickel, there is a high preference on small particles as their gas proportions remain high (>80%) even in high particle concentrations. Both nickel and antimony had highly varied, inconsistent, and even many negative reduction rates. Zinc would be classified in the midrange, but due to its increase in gas proportion in case K4 concerns for large measurement inaccuracies emerge and it is left unclassified.

Class III behavior was observed for both mercury and bromine. They both had consistently very high (>90%) gas proportion, which is expected. This indicates that there are very little adsorption phenomena between particle matter and gaseous class III elements. Bromine has a very high (>0.85) reduction rate in all cases, but mercury reduction rates are primarily negative, due to measurement inaccuracies. Case K1 provides an acceptable (0.52) reduction rate for mercury. The three process parameter changes between cases are very difficult to identify. This is caused by failed mercury calculations in other cases and by conflicting reduction rates for cobalt in cases K3 and K4. There was an expected decrease for mercury reduction between cases K1 and K2, but it was not possible to identify. Cobalt has a steady reduction rate in both cases K1 and K2, and an expected increase is identified between cases K2 and K3, but a further increase was not present between cases K3 and K4. Instead, a noticeable decrease was found, which only raises more concerns regarding measurement accuracy in general.

6.3.3 Comparative analysis of measurement results

This subchapter focuses on comparative analysis of the measurement campaign. Analysis is performed by using similar histograms and scatter graphs in Figures 24 – 28 in accordance with the analysis plan. In addition to finding correlations, grouping behavior is investigated by comparing histograms in Figures 17 and 24. Figures 24 – 27 are similar to figures used in subchapter 4.2 (Figures 17-20). Figure 28 is an addition, which is used to investigate heavy metal reduction cut-off rates. In addition, appendix A3 and A4 data on heavy metal gas proportion and distribution in condensate is used to briefly describe heavy metal speciation in flue gas and condensate.

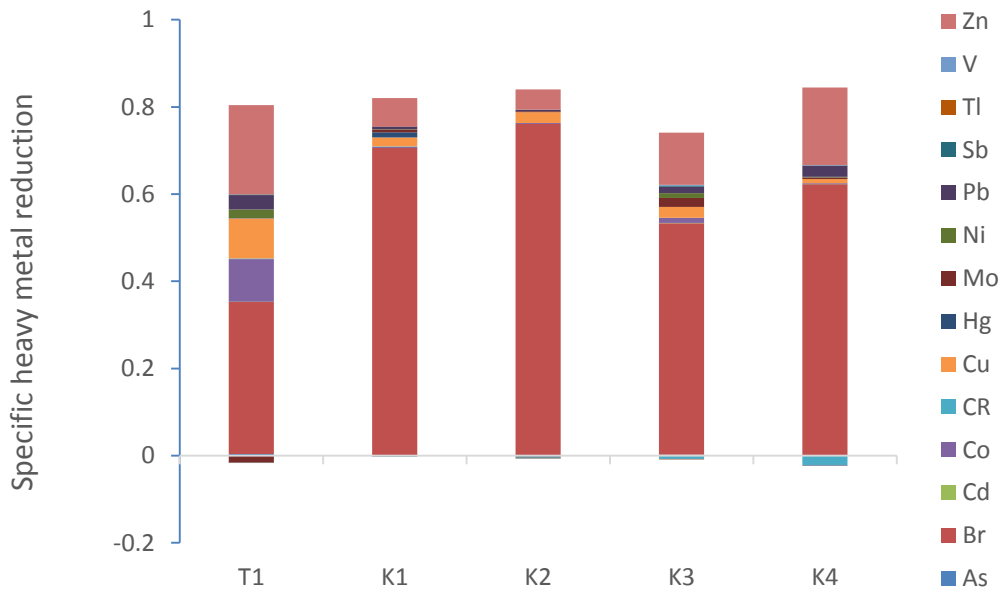

Figure 24: *Total and specific heavy metal reduction*

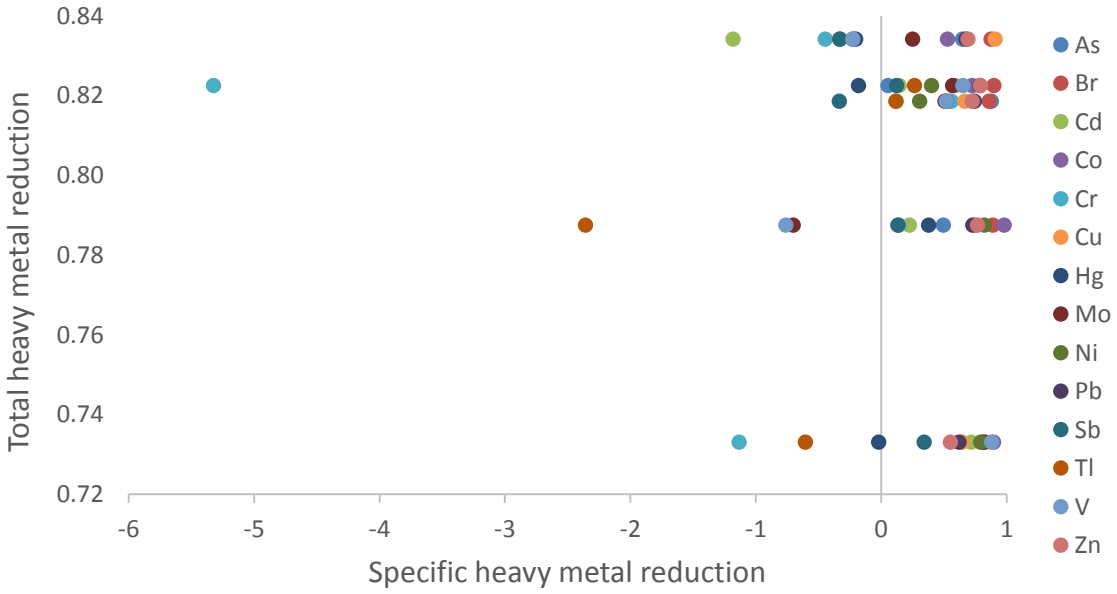

Figure 25: *Total and specific heavy metal reduction correlation graph*

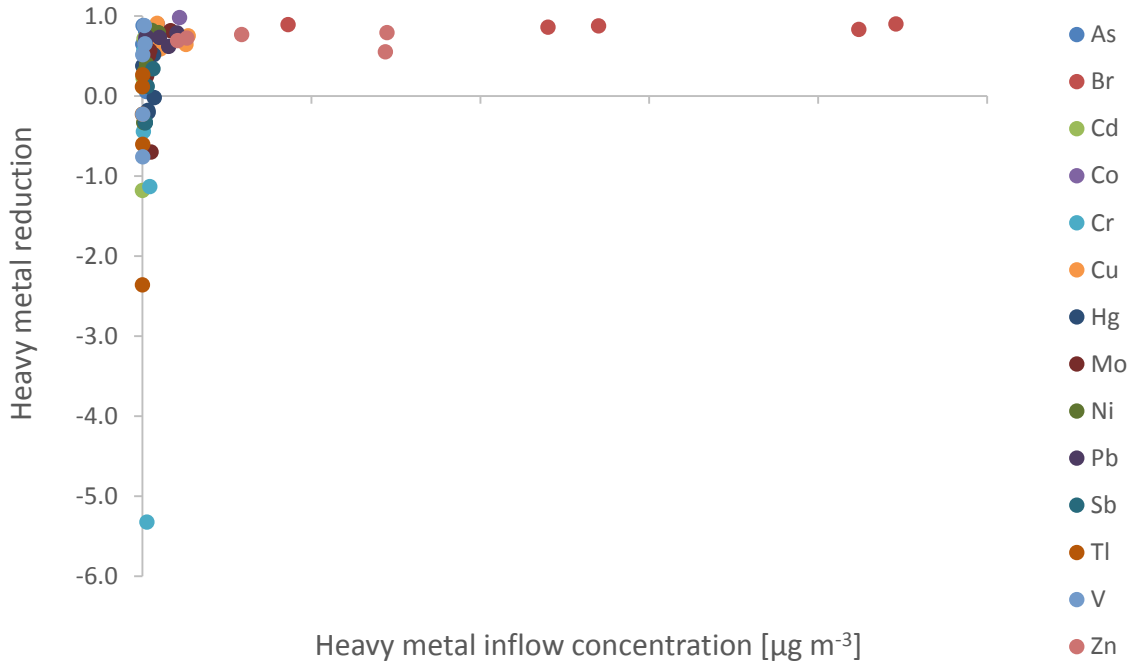

Figure 26: *Specific heavy metal reduction and inflow heavy metal concentration correlation graph*

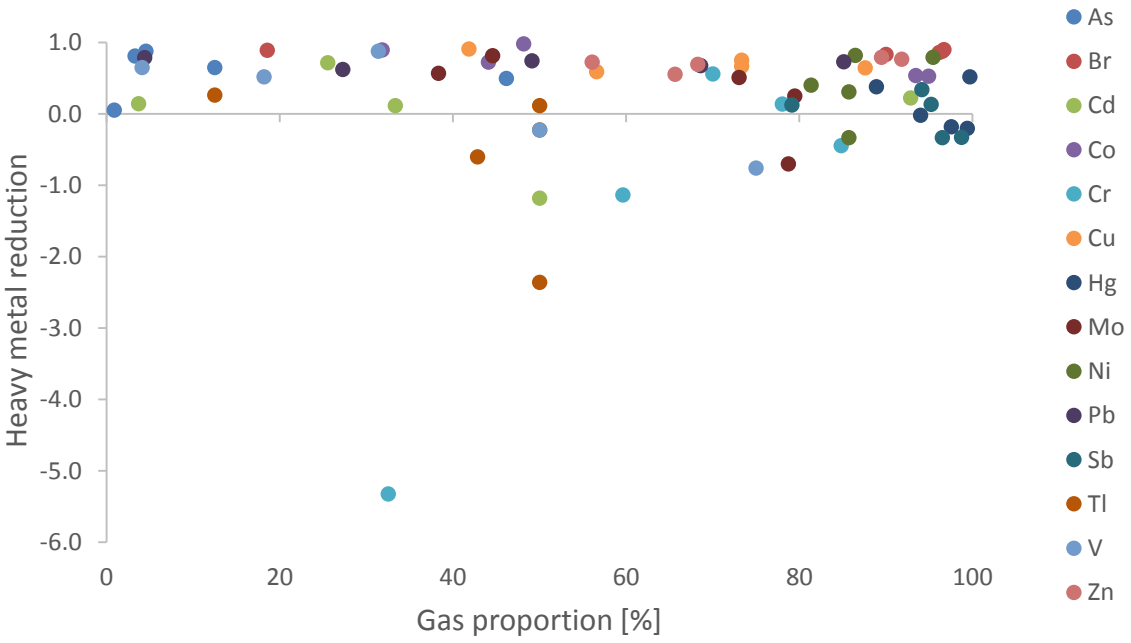

Figure 27: *Specific heavy metal reduction and gas proportion correlation graph*

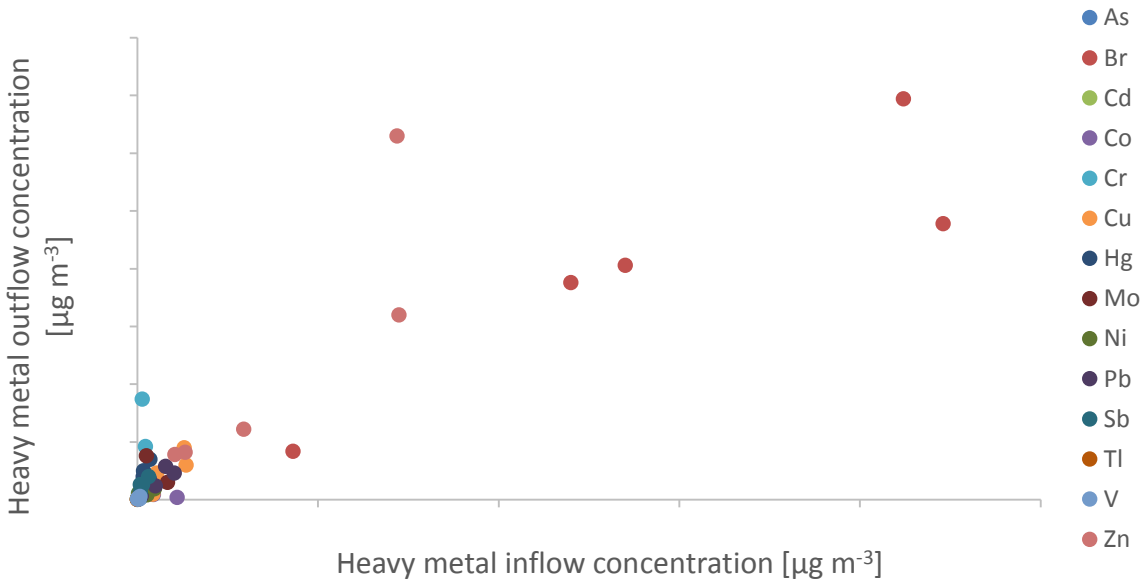

Figure 28: *Inflow and outflow heavy metal concentration correlation graph*

Figures 24 – 28 present a similar situation as in subchapter 4.2. No clear correlations or grouping behavior emerges in these figures. All measurement cases were lumped in these figures to try and find specific grouping behavior, at least between the two power plants, but also for high particle load cases (K3 and K4). Due to measurement inaccuracies, low heavy metal concentrations in flue gas, prevalent detection limit values, and changes in power plant operating parameters correlations expected behavior cannot be clearly identified using the measurement data available. Although comparability between cases and power plants is very high, due to excellent support data and operating parameters, clear differences between cases fail to emerge. Despite vastly different pre-control systems, boiler and fuel type, and significant changes in power plant operating parameters, each case seems to blend into the scatter figures. This knowledge again leads to concerns about measurement accuracy and the feasibility of the used measurement approach in determining heavy metal reduction in later-stage flue gas control systems.

Figure 24 presents a similar view of dominant reduction species in comparison to previous measurement data. Reduction rate of bromine is the most significant in all cases, but its proportion is smaller than for power plant 1. When comparing measurement case T1 with other waste incineration plants, some similar behavior can be observed. A small, but noticeable copper reduction is present in all cases, and power plant 3 shares a similarity with zinc reduction with case T1 as well. The cobalt reduction present in case T1 cannot be observed in power plant 1 or 3 measurements. For power plant K a significant zinc reduction exists in all cases, and its relative amount is increased with particle load. Similar zinc reduction is found in power plant 2 and 6 measurements. In addition, a somewhat noticeable lead reduction is present in both previous measurement data power plants and power plant K. In smaller particle load conditions copper reduction is larger

than lead reduction, but in higher particle load this is reversed. An expected difference, between reduction ratios of plant T and K was also found. In power plant K total reduction rate is mainly dominated by two species, bromine and zinc, but power plant T has a more varied range of species making up its total reduction. This may indicate a greater variability in fuel composition, which applies in this situation, but drawing any further conclusion would require more measurement cases. Also, cases excluding K3 have similar total reduction rates. The only difference between other cases was that case K3 had a significantly shorter measurement time, which could explain a lower total reduction rate and more varied reduction species constitution. Shorter measurement time increases the errors caused by changes in power plant operating parameters. This may explain the slight differences in reduction, but they could also be attributed to measurement inaccuracies and low concentrations in samples.

Figures 25 – 28 use scatter graphs to evaluate heavy metal speciation, reduction, and overall grouping behavior between power plants, although only two plants were used in this study, some grouping behavior based on controlled plant parameters was also expected. Figure 25 purpose is to investigate the overall quality of the measurements by trying to determine whether higher total reduction rate leads to more realistic reduction rates, i.e. non-negative values. Figures 26 and 27 were used to find correlations in specific heavy metal reduction and some certain parameter, in these figures the parameters are inflow concentration and gas proportion, respectively. An increase in reduction rates for all heavy metal species was expected when inflow concentrations increase. This correlation is considered to occur, due to the fact that higher inflow concentration reduces measurement inaccuracies and detection limits, which will in return provide reduction values closer to particle matter reduction (class I & II heavy metals). Figure 27 is also used to investigate the accuracy of class I & II heavy metal gas proportions and reduction and to investigate class III element composition in the flue gas. Finally, Figure 28 is used to identify cut-off limits.

Figure 25 did not provide any correlation between total reduction rate and the accuracy of measurement results, since in all cases there are negative specific reduction values. In previous measurement data a correlation was found, but in this figure it can be clearly seen that no such correlation exists. This can be caused by a smaller data sample in this figure, but definitive answer would require more data. Figure 26 did not provide any believable correlation between inflow concentration and reduction. Only bromine, nickel, and cobalt showed a slight increase in reduction, but other heavy metals did not correlate at all. Cobalt showed the largest increase, which could be caused by its class I status, since particle reduction rate also increases with inflow concentration. A rough estimate was made for inflow concentration limit, which separates negative reduction values. This limit is approximately 5 $\mu g\ m^{-3}$ according to this data. Bromine data points formed a straight line with a small increase in high concentration area. This may indicate that bromine concentrations were high enough for near optimal reduction.

Figure 27 either formed fluctuation or straight lines for class II & III heavy elements, and a small inverse correlation between class I heavy metal reduction rate and gas proportion. Fluctuations can indicate two possibilities, different condensation behavior between measurement cases or measurement inaccuracies. Due to a lack of measurement cases and larger inflow concentrations, it is impossible to separate these possibilities based on this graph. Straight lines are more likely to represent systematic measurement errors, due to theoretical understanding. As gas proportion increases heavy metals will either be found condensed or adsorbed on small particle matter or in gaseous phase. Due to significantly different reduction mechanisms, a change in reduction behavior is expected, but not found. Figure 28 was expected to show rising plots plateauing at a cut-off point, but such behavior is not present. Bromine and zinc form rising plots that curve back down at a certain point. This does not pass as cut-off point behavior, since reduction mechanisms are not expected to have behavior that will hinder heavy metal reduction, instead an equilibrium will be reached in the case of gas solubility and for particle reduction particle size cut-off rates were defined in chapter 2.3.

Appendix A3 is used to investigate changes in gas proportion before and after the reduction process. A typical change in gas proportion for class I & II heavy metals is a significant increase that should correlate with reduction rate. This correlation with reduction rate was preliminary investigated with Figure 27, but the quality of the data prevented proper correlation formation. First by observing class I heavy metal behavior through gas proportion and reduction rates, it can be identified that in most cases gas proportion doubled in cases T1 and K3, only slightly changed in cases K1, K2, and K4. Cases T1, K3, and K4 all had reduction values between 0.7 and 0.98 and gas proportions before the scrubber under 50%. While in cases K1 and K2 reduction rates were near 0.5 and gas proportions before the scrubber were over 90%. In addition, gas proportions decreased to values between 70% - 80% after the scrubber, which is contrary to current understanding. Before drawing conclusions from gas proportion and its change correlating with reduction rates, it has to be stated that detection limits and measurement inaccuracies can easily discredit this finding. Class II heavy metals have similar behavior where gas proportion increases in the wet scrubber, which is supported by having smaller particles slipping into the gas phase measurement system, but not by reduction rate values. By using vanadium as an example, it can be seen that large changes in gas proportion do not correlate with high reduction rates. In cases K1 and K2 reduction rate of vanadium is negative, but a similar change in gas proportion takes place in all cases. Such behavior is prevalent in other class II heavy metal behavior as well. One interesting finding among class II heavy metal species was the decrease in arsenic gas proportion in the T1 case.

Arsenic had a typical reduction rate and no detection limit values were used in its calculation. This significant change in gas proportion could be caused be gaseous arsenic compounds dissolving in the scrubbing liquid. This would explain the relatively high

reduction rate and change in gas proportion. In chapter 4.1 the reduction rate for gaseous arsenic was described. Gaseous arsenic reduction rate is high enough to reach the proposed reduction, but case T1 calculations found that arsenic mass balance deviation is very large. Similar behavior in regards to gas proportion change can be found for lead in case K2 and for cadmium and nickel in case K4. Lead and nickel have also a significant reduction rate to achieve a relevant reduction, but nickel mass balance deviation is very large and the deviation for lead is also considerable. Faced with these uncertainties no actual conclusions can be drawn on possible gaseous class II heavy metal compounds. Also, according to (Cordoba, et al., 2012), all class II heavy metals are particle-bound, except for arsenic, which only had 2% gas proportion. Class III behavior for mercury was expected, since gas proportions were very high and changed only slightly in the wet scrubber. For bromine, the changes were more pronounced as there was a significant decrease in gas proportion. This indicates that gaseous bromine is more easily captured than bromine on the particle matter.

Using appendix A4 data is difficult due to detection limit values, but zinc can be used as a reference in determining sensitivity behavior between heavy metal precipitation and pH. Scrubbing liquid pH was changed from 5.5 to 7 between measurement cases K1 and K2. In cases K3 and K4 pH was also at 7. By comparing dissolved proportions for zinc from cases K2 – K4 to case K1, a reduction in dissolved proportion can be clearly identified. Dissolved proportion of zinc values in case T1 are significantly different from both case K1 and cases K2 – K4, which is expected due to differences in power plant design, thus comparisons are unfeasible. The same pattern cannot be identified for molybdenum, copper, chromium, and cobalt, since dissolved proportions seem to fluctuate near similar values in all cases. According to (Li, et al., 2013) a link between pH and heavy metal precipitation exists, but it cannot be clearly determined for all selected heavy metals. Similar detection limit values were also prevalent, particularly in publication (Ohki, et al., 2011).

6.3.4 Overall reduction efficiency analysis

Reduction coefficients for lumped model –tool have been calculated twice in chapter 4 and the third investigation is carried out here. Overall reduction efficiencies are evaluated using similar data filtering methods as in subchapter 4.2. Only Novel 2 approach is altered by only filtering values that are used in inaccurate mass balance calculations. The Average approach only filters negative reduction efficiencies, Novel 1 approach eliminates reduction rates near zero (<0.1), and Novel 2 approach removes inaccurate mass balance values. Reduction coefficients are presented in Table 25 and are calculated based on reduction values from Tables 20 - 24. These values can be used in the lumped model –tool as reduction coefficients, but it has to be stated that these values are averaged from a small sample of data and they should be used to supplement reduction values acquired from the previous measurement data survey (Table 16).

Table 25: *Reduction coefficients acquired from measurement campaign*

Filtering method	Particle matter (PM)	Arsenic (As)	Bromine (Br)	Cadmium (Cd)	Cobalt (Co)	Chromium (Cr)	Copper (Cu)	Mercury (Hg)
Average	0.778	0.578	0.872	0.301	0.734	0.349	0.712	0.448
Novel 1	-	0.709	0.872	0.301	0.734	0.349	0.712	0.448
Novel 2	-	0.728	-	0.184	0.597	0.140	0.633	0.448
Filtering method	Molybdenum (Mo)	Nickel (Ni)	Lead (Pb)	Antimony (Sb)	Thallium (Tl)	Vanadium (V)	Zinc (Zn)	total
Average	0.536	0.398	0.712	0.199	0.191	0.683	0.706	0.799
Novel 1	0.536	0.581	0.712	0.199	0.191	0.683	0.706	0.799
Novel 2	0.632	-	0.680	0.199	0.265	0.765	0.672	-

Comparisons can be drawn between data from selected heavy metal reductions for previous measurement data survey and measurement campaign (only for average and novel 1 methods). Particle reduction is very similar in both, but total reduction is much higher in measurement campaign data. Significantly larger reduction rates in Table 25 can be found for arsenic and copper. Lead, zinc, nickel, and cobalt have similar reduction values. The rest are significantly (<0.2) lower in comparison to Table 16. Such differences are expected and likely caused by a smaller sample size (5 cases). A recommended use of Table 16 and 25 reduction values in the lumped model –tool is to use higher values for general rough design and calculation guarantees for special plants using the lower values. Average method values are not suggested to be used at all, but both novel 1 and novel 2 values have reasonable filtering to provide a rough estimate on heavy metal reduction.

By comparing fluctuation of heavy metal reduction values between data filtration steps, measurement accuracy can be investigated through a stochastic method. No major fluctuations appear, but in the case of arsenic, cadmium, cobalt, chromium, and nickel a noticeable change can be found. For arsenic and nickel fluctuations take place between each step and changes are significant, especially for nickel. For cadmium, chromium, and cobalt only the last step causes fluctuation, which is caused by mass balance deviations. Because mass balance deviations are so prevalent in novel 2 method, it should be treated as an extremely rigorous filtering step. All other heavy metal species do not fluctuate in any significant way. Reduction values for class I heavy metals (cobalt) are quite well in line with particle reduction up to novel 2 filtering. Most class II heavy metals have reduction rates lower than particle and total heavy metal reduction, which may indicate heavy metal condensation behavior favoring smaller particles, but can easily be caused by measurement inaccuracies. Using this approach cadmium, chromium, anti-

mony, and thallium would be prime candidates in class II heavy metal condensation investigation. Class III compounds presented typical reduction values and were completely free of fluctuation.

6.4 General discussion of measurement campaign

6.4.1 Challenges in measurements

Overall issues in this measurement campaign can be divided into three different categories: mass balance measurement concept, power plant and process operations, and measurement accuracy. Mass balance measurement concept suffered from problems during data analysis, due to most of the calculated mass balances having wide deviations in their values. This can be attributed to measurement inaccuracies, but another concern rises: compatibility of flue gas and condensate measurements. There are numerous problems in combining measurement data from these two very different sampling methods. The major issues in combining data are greatly different sampling methods and different subcontractors used for sample analysis. Heavy metal samples from flue gas were gathered with a probe during the whole measurement case time, but condensate samples were taken during a short window of time in the middle of the measurement case. This difference in sampling is a major drawback in this campaign and its effects are evident in data analysis.

Systemic issues in selected power plants (T and K) that appeared during the measurement campaign caused some concern. First issue involves the amount of heavy metals in flue gas entering the scrubber. When choosing a plant with higher heavy metal concentrations in fuel (power plant T) the flue gas control systems before the wet scrubber are so efficient that concentrations are hard to detect. Similar problem arises in plants that have less-intensive flue gas pre-control, but also lower heavy metal concentrations in fuel (power plant K). This leads to the same issue as in the other case. Also there is a problem with process parameter fluctuations and rigid requirements. Power plant T had very steady operating parameters during the measurement case time, but due to rigid requirements no process alterations were allowed between cases. A reverse problem arose in power plant K, where changes to process parameters between cases were allowed, but many parameters were adjusted during the measurement case time, which lead to spiky and fluctuating plant operating values. Finally, the typical issue when measuring small concentrations, detection limits and measurement accuracy was also a great concern in this measurement campaign. This is unavoidable in both ordinary power plants and waste incinerators, which leads to a need for more accurate and continuous measurement systems for selected heavy metals. In comparison to measurements conducted in (Cordoba, et al., 2012), this measurement campaign produced rather poor results and values in terms of mass balance calculations. Reasons for such success in the publication can be attributed to the combination of somewhat heavy metal laden fuel

and less-intensive flue gas control systems before the scrubber. Also, more sampling points (scrubbing chemical, feed-in water) were used.

6.4.2 Future prospects and summary

In order to improve future measurement campaigns, many steps can be taken in the planning stage to try and improve the quality of the data. First and foremost, a stable and controllable power plant is required. This means that during measurement cases all process parameters can be kept very stable, but between cases many parameters can be changed in a relatively quick manner. This would lead to an improvement in data accuracy and increase in reduction correlation understanding, since more measurement cases can be performed in different operating parameters. One significant issue was the low concentrations of heavy metals in flue gas entering the scrubber. This can be avoided by having a greater control over flue gas pre-control systems, for example reducing electric current in ESPs and bypassing fabric filters. It is also important to select a fuel that has significant heavy metal concentrations and species variation. Improvements can be conducted on the measurements themselves. For example, taking proper particle matter samples and forming a particle size distribution graph and grouping particles by their size. Then, try to analyze these groups for heavy metals. This would increase understanding in class II heavy metal condensation behavior. A less complex method for improving heavy metal condensation understanding would be to analyze electrostatic precipitator and fabric filter particle size and heavy metal concentrations. This way a rough understanding could be formed between particle size and heavy metal species. Heavy metal reduction measurements could be greatly improved by using continuous measurements for both gaseous oxidized and elemental mercury, this measurement data would greatly improve understanding in mercury behavior in flue gas and its reduction behavior.

In summation, this measurement campaign involved two power plants and a total of five measurement cases. Measurements were taken from the flue gas before and after the wet scrubber and condensate flows leaving first and second scrubber stages. These values were used to calculate heavy metal mass balances for flows entering and exiting the wet scrubber. These mass balances proved to be quite inaccurate and brought the whole concept into question. Also, reduction rates and gas proportions were calculated for heavy metal species with some success. Grouping and correlation behavior for heavy metal reduction was investigated, but nothing definitive was discovered. In addition, a comparative analysis between this measurement campaign and previous measurement data was conducted and it led to some similarities. Finally, reduction coefficients were calculated for lumped model –tool by using similar data filtration methods as in subchapter 4.2. Measurement campaign suffered from issues including measurement inaccuracies, compatibility of mass balance measurements, process parameter limitations, and fluctuations.

7. CONCLUSIONS

Heavy metal reduction in wet flue gas scrubbers was examined from 4 different aspects: theoretical approach through literature survey, calculation tools, and a practical approach through measurement data survey and measurement campaign. Each approach tried to test and support the findings in previous steps and thus focus of later approaches was heavily influenced by earlier findings.

Literature study was conducted by investigating the reasons, phenomena, and methods in heavy metal reduction in wet scrubbers. EU directives present emission limits on flue gas and wastewater heavy metal concentrations and health effects included carcinogenic behavior, serious organ damage, and neural damage. Classifications for heavy metal speciation were identified based on volatilization and condensation behavior before wet scrubbers. After the behavior research, the physical and chemical reduction mechanisms and their theoretical sensitivity were successfully investigated. Physical mechanisms included solubility for gases, inertial collision methods for large particles, and diffusion for smaller particles. Chemical reduction mechanisms included sulfur and hydroxide based precipitation for most heavy metals and multiple oxidation and complexation pathways for mercury. Finally, an interesting re-emission behavior for mercury was presented, where oxidized mercury was reduced back into its elemental form. To investigate the methods of heavy metal emission control, some wet scrubber types and their support processes were presented. Their applicability and limitations were also identified and an additional small particle control system was discovered: condensation scrubber.

Calculation programs were investigated to find or create a modeling tool, which could predict the whole heavy metal behavior process from speciation and classification behavior to chemical reactions in scrubbing liquid. Three different ideas were tested to fulfill a part of this goal. First a simplified kinetic and thermodynamic approach to mercury speciation, reduction, and complexation was conducted, but due to great problems early on it was not expanded. The tool managed to provide useful system for discovering possible reaction pathways to support more detailed kinetic modeling. Major issues were found in thermodynamic and kinetic data availability, unreliability of reaction pathways, incompatibilities between kinetic and thermodynamic calculations. Next, two commercial calculation programs (Aspen plus & Chemcad) were tested only to model reduction behavior. Challenges were quickly identified: a lack of important heavy metal compounds, scrubber types, and poor calculation fidelity of solid stream interaction. These programs only managed to provide useful information in regards to particle matter reduction in few select scrubber types. Finally, a modeling tool based on a lumped

modeling approach was created. It lumped specific heavy metal reduction phenomena to a simple reduction rate constant. Issues in lumped tool –model consist of its base idea of having reduction coefficients. These coefficients are typically received from measurement data; thus they are either averaged or plant specific values.

Measurement data surveys were conducted to provide a more practical background for theoretical knowledge and to support the analysis of measurement campaign results. Surveys produced mixed and uncertain results, due to a lack of supporting data and different power plant design. Clear comparisons between results were difficult or impossible to draw in both surveys. This led to poor correlation and grouping of various investigated power plants. In addition, the lack of a large supply of measurement data made averaged reduction efficiencies somewhat unreliable. Survey on previous measurement data proved to be more successful, but due to lacking data no mass balances were calculated. Despite all adversities, reduction coefficients for lumped model –tool were created.

The measurement campaign was the pinnacle of this thesis and its goal was to provide precise and comparable measurement data and investigate heavy metal reduction rate sensitivity parameters, possible cut-off concentrations, and provide more accurate reduction coefficients for lumped model –tool. The campaign failed to properly evaluate sensitivity parameters and cut-off concentrations, due to measurement inaccuracies and large mass balance deviations. Also, calculated reduction coefficients are only somewhat reliable due to lack of a large pool of samples and previously stated issues. In some cases, measurement campaign managed to provide useful behavioral data for selected heavy metals, for example phase, adsorption, and condensation data. Measurement campaign results were compared with data survey results and some similar reduction behavior was discovered, but not properly validated.

Future research can be divided into two categories: modeling and measurements. Modeling challenges include developing a fully-fledged kinetic tool for mercury speciation and reduction in various flue gas control devices. This tool could also be expanded into multiple different directions: computational fluid dynamic modeling, special sorbent and oxidizer kinetics or multi-pollution behavior and control (NO_x & SO_2) modeling. In addition, building a calculation platform for class I & II heavy metal speciation and reduction is an important goal in heavy metal pollution research. Future measurement campaign could investigate elemental and oxidized mercury speciation, reduction, and binding in different flue gas control systems and power plants. In addition, a measurement campaign investigating class II heavy metal condensation behavior on particle matter, with a focus on trying to find correlations between heavy metal species and particle size, flue gas moisture and particle reduction, and further classifications within class II heavy metals.

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APPENDIX

A1: Complete table of reduction efficiencies used in chapter 4.2. (g stands for gas and p for particle). Red cells are reduction rates, which are negative and orange stands for calculations performed using detection limit values.

	1	2a	2b	2c	3a	3b	3c g	3c p	3d g	3d p	3c tot	3d tot	4a g	4a p	4a tot	4b	4c	4d	4e	5 g	5 p	5 tot	6
PM	0,86	0,99258	0,375	0,93719																		0,91	
As	0,87143	0,68657	0,05	0	0,438	0,8014	0,5		0,33333	0,9697	0,4	0,9697	0,17829	0,89021	0,94044	0,333	0,238	0	0,294	1	0,54808	0,69872	0,75294
Br	0,98182																						
Cd	0,625	1			0,5625	1			0,92308	1	0,53846	1	0,78473	0,82302	0,78969					-1,7115	0,54808	0,22527	0,79412
Co	0,83333	1			0,438	0,8014	0,15385	0,7931	0,57143	0,5	0,37037	0,72973	0,17829	0,63551	0,64964					-5,3269		-5,3269	0,79412
Cr	0,91724	0,28571	-0,4375	1	0,438	0,8014	0,21429	-0,6667	0,9	0,75556	0,77586	0,51852	0,82544	-0,0378	0,40421	-0,006	0,268	0,952	0,693	0,51795	0,45769	0,49385	1
Cu	0,74063	0,32847	-2,934	0,75641	0,438	0,8014	-0,8049	0,41558	0,86364	0,95679	0,4106	0,88277	-0,5225	0,55495	0,15038	0,167	0,043	0,468	0,599	0,23887		-0,9504	0,93137
Hg	0	0,68182	-0,5714	0,18182	0,8655	0,9043	0,85081	0,84271	0,93252	0,98276	0,86549	0,90432	-0,1225	0,36791	0,35599	0,714	0,375	0	-0,5	-0,8077	0,65237	0,54808	0,79412
Mo																							
Ni	0,92973	1	1	0,13333	0,438	0,8014	0,4	0,11111	0,54	0,46552	0,5	0,41791	0,84276	0,33844	0,68012	0,661	0	0,928	0,901	0,58916	1	0,6772	0,97941
Pb	0,65714	0,67987	0,13333	0,7033	0,438	0,8014	-2,5	0,50633	0,82888	0,83562	0,04082	0,72	-1,6873	-1,3932	-1,6275					0,89263	0,93866	0,90421	0,8877
Sb	0,09804									0,75		0,75	0,19774	0,19774	0,19774						1	-0,8077	0,79412
Tl	0,6				0,5625	1			0,66667		0,66667		0,19774	0,19774	0,19774						1	1	0,79412
V	0,925	1			0,438	0,8014			1		1												1
Zn		0,90625	1	1			-0,5041	-0,6828	0,49853	0,68755	0,30641	0,54294	0,32729	0,49985	0,48178	0,87	-0,484	0,714	0,692	0,2737	0,43432	0,42376	0,87193
tot	0,939	0,79356	-0,5472	0,7489	0,50565	0,85141					0,51	0,76613			0,39965							0,66987	0,87237

A2: Complete table of gas proportions used in chapter 4.2 (before and after stand for measurements before and after scrubber). Orange stands for calculations performed using detection limit values.

Gas %	1 before	3c before	after	3d before	after	4a before	4a after	5 before	after
PM									
As	0,70922	40	33,3	0	0	11,7859	50	33,3333	0
Br									
Cd	0,49751	0	83,3	0	-	87,055	89,1068	14,2857	50
Co	13,0435	48,1	64,7	78,4	60	30,7274	50	100	100
Cr	3,78007	18	63,5	16,7	57,7	51,206	15,0033	60	57,1429
Cu	0,14388	27,2	83,1	13,7	68,2	37,5505	67,2878	100	39,0244
Hg	83,3333	82	91	56	92,1	96,8361	98,1935	7,14286	28,5714
Mo									
Ni	2,43902	28,6	34,3	13,4	20,5	67,7499	33,3027	78,5714	100
Pb	0,89723	23,7	86,4	35,1	61,9	79,6447	81,4595	74,8368	83,8863
Sb	0,59642	-	33,3	0	0	50	50	0	100
Tl	1,96078	0	0	-	0	50	50	0	-
V	2,43902	0	-	-	-				
Zn		19,2	41,6	10,6	38,9	10,471	13,5926	6,56891	8,27967

A3: Gas proportion values acquired from the measurement campaign. Red cells are gas proportions calculated with detection limit values. Cells under power plant ID represent inflow gas proportions and next to them are outflow proportions.

Gas proportion [%]									
T1		K1		K2		K3		K4	
46,1538	2,38095	4,54545	0	12,5	0	3,2967	11,7647	0,9009	0,9009
18,5615	72,2222	96,1538	71,2766	96,5108	63,5468	90,0094	58,2133	96,6876	45,6067
92,8571	94,1176	33,3333	60	50	50	25,5319	30,7692	3,7037	2,04082
48,1818	97,4359	93,4426	84,375	94,9153	73,5294	31,8182	80	44,086	44,4444
78,0488	96,8254	70	55,5556	84,8485	80,7692	59,633	94,2982	32,5397	82,9545
73,3333	86,0927	73,3333	94,1176	41,8605	57,1429	87,5969	93,5412	56,6038	83,3333
88,8889	80	99,6979	99,4475	99,4152	99,2063	94,0171	99,1501	97,561	99,0099
78,7402	82,2281	73,0337	81,3725	79,4872	78,0702	44,5783	71,4286	38,326	34,6535
86,4662	95,2381	85,7143	88,6364	85,7143	82,1429	95,4447	84,375	81,3559	40,7895
85,1485	96,4912	49,1228	46,875	68,6047	38,2353	27,2727	62,069	4,38247	29,5154
95,2381	99,2366	96,5116	99,2366	98,75	99,2366	94,1558	98,5222	79,1367	82,7068
50	85,7143	50	50	50	50	42,8571	40	12,5	14,2857
75	90,9091	18,1818	83,3333	50	83,3333	31,3725	72,7273	4,10959	11,1111
91,8367	92,3825	56,0606	62,5	68,2692	61,5385	65,6467	86,0759	89,5028	62,5

A4: Complete table of dissolved proportions in condensate received from the measurement campaign. Labels 1 and 2 stand for scrubber stages. Red cells are values over 100% and orange cells are used for calculations performed with detection limit values.

	T1		K1		K2		K3		K4	
	1	2	1	2	1	2	1	2	1	2
As	100	100	33,3333	100	33,3333	100	33,3333	100	50	100
Br										
Cd	100	100	100	100	100	100	100	100	57,1429	100
Co	100	100	78,9474	100	96,1538	100	107,692	100	81,8182	100
Cr	50	100	20	100	26,8293	100	22,2222	100	35,7143	12,5
Cu	100	100	80	100	66,6667	50	83,3333	50	87,5	100
Hg	100	100	1900	16,6667	400	100	170	50	229,73	200
Mo	33,3333	100	50	100	50	50	45,4545	50	50	50
Ni	100	100	73,5294	20	2400	20	90	100	102,273	100
Pb	100	100	25	100	33,3333	100	50	100	14,2857	100
Sb	100	100	100	100	100	100	100	100	100	100
Tl	100	100	100	100	100	100	100	100	150	100
V	100	100	100	100	100	100	100	100	100	100
Zn	78,5714	25	80	53,8462	28,866	33,3333	34,8485	12,5	32,3077	23,0769